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Preparation, Substitution Reactions, and Kinetic Studies of Chromium and Tungsten Thiocarbonyl Complexes

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Chromium and tungsten $M(CO)_5(CS)$ complexes are prepared by reaction of reduced metal carbonyl species with thiophosgene, Cl_2CS. These products undergo carbonyl substitution by donor ligands (PPh_3, pyridine, I^-, Br^-, Cl^-) to give largely *trans*-$M(CO)_4(CS)(L)$ products and, in some cases, smaller amounts of the cis isomers. Kinetic studies show that rates of both the dissociative (SN1) and associative (SN2) pathways involved in the PPh_3 substitution reaction of $W(CO)_5(CS)$ are much faster than PPh_3 substitution in $W(CO)_6$ under the same conditions. The reaction of $W(CO)_5(CS)$ with I^- to form [*trans*-$W(CO)_4(CS)(I)]^-$ proceeds by an associative mechanism also at a rate which is much faster than that of the analogous reaction of $W(CO)_6$. Abstraction of the halide ion from [*trans*-$W(CO)_4(CS)(I)]^-$ with Ag^+ followed by ligand (PPh_3 or ^{13}CO) introduction gives a *trans*-$W(CO)_4(CS)(L)$ complex. Addition of 2,2'-bipyridyl in this reaction gives $W(CO)_3(CS)(bpy)$. The $Cr(CO)_3(CS)(diphos)$ and $W(CO)_3(CS)(diphos)$ complexes have been prepared by heating $M(CO)_5(CS)$ with $Ph_2PCH_2CH_2PPh_2$. The $W(CO)_3(CS)(diars)$ complex has been made similarly using *o*-$C_6H_4(AsMe_2)_2$. Heating $W(CO)_3(CS)(diphos)$ at 195 °C with more diphos results in the replacement of two additional CO groups to give $W(CO)(CS)(diphos)_2$. The results indicate that CS is much more inert to substitution than CO and that the CS ligand accelerates the rate of CO substitution in $W(CO)_5(CS)$ as compared to that observed in $W(CO)_6$.

Introduction

Earlier we communicated the preparation and some preliminary results of substitution reactions of chromium and tungsten $M(CO)_5(CS)$ complexes.[1-4] The present paper provides details of these reactions and reports significant results of other substitution reactions of these complexes.

These group 6 $M(CO)_5(CS)$ complexes were expected to undergo photochemical and thermal carbonyl substitution reactions similar to those of the $M(CO)_6$ complexes. Since studies of other thiocarbonyl complexes suggested that the thiocarbonyl ligand is bound more strongly to the metal than carbonyl ligands,[5] it was anticipated that carbonyl substitution, rather than thiocarbonyl replacement, would be observed. However, the mechanism of substitution and geometries of the products could not be predicted a priori, since little was known about the chemistry of metal thiocarbonyl complexes and no similar simple carbonyl thiocarbonyl complexes were known.

Results

Preparation of the $M(CO)_5(CS)$ Complexes. Reduced group 6 carbonyl species were prepared by stirring and refluxing tetrahydrofuran (THF) solutions of the $M(CO)_6$ complexes with sodium amalgam for 12–18 h, a process which appears to give mainly the $M_2(CO)_{10}{}^{2-}$ dianions.[6] Reaction (see eq 1) of these solutions with excess thiophosgene gives

$$M(CO)_6 \xrightarrow[(2)\ Cl_2C=S]{(1)\ Na/Hg,\ THF} M(CO)_5(CS) \qquad (1)$$

low but reproducible yields of the $M(CO)_5(CS)$ complexes. The yields of $M(CO)_5(CS)$ in small reactions (1–10 g of $M(CO)_6$ starting material) are in the range of 3–6% for chromium and 10–15% for the tungsten product, based on the $M(CO)_6$ complex. Scaling up the reactions to 30–50 g of $M(CO)_6$ gave somewhat reduced yields of $Cr(CO)_5(CS)$ (2–4%) and $W(CO)_5(CS)$ (6–9%). The $Mo(CO)_5(CS)$ complex could also be detected in similar reactions of $Mo(CO)_6$, but only small reactions (~1 g of $Mo(CO)_6$) yielded significant amounts of this thiocarbonyl complex. A large amount of $M(CO)_6$ is also regenerated in all of these preparations; from 1 to 8 times as much $M(CO)_6$ as $M(CO)_5(CS)$ is produced. Other products which may be formed in these reactions have not been thoroughly investigated.

Sublimation of the evaporated reaction mixtures thus obtained yields yellow crystals composed of $M(CO)_5(CS)$, $M(CO)_6$, and traces of other impurities. The separation of the $M(CO)_5(CS)$ products from the hexacarbonyl complexes was found to be a difficult process because of the similar physical properties of the complexes. There was little evidence of separation during sublimation or column chromatography of the mixtures. Crystallization of the mixtures from pentane or hexane solutions by slow cooling (1–2 days) was found to be a practicable, although lengthy, separation method. Crystals thus formed contained large amounts of $M(CO)_6$, along with some $M(CO)_5(CS)$. After four to six crystallization steps most of the $M(CO)_6$ had been removed, leaving in solution a relatively small amount of $M(CO)_5(CS)$ of approximately 99% purity. Gas–liquid chromatography gave excellent separations of the $M(CO)_5(CS)$ and $M(CO)_6$ complexes, presumably because of the greater solubility of the thiocarbonyl complex in the liquid phase. Thus very pure $W(CO)_5(CS)$ and $Cr(CO)_5(CS)$ (>99.95%) were attainable in small quantities through preparative gas chromatography. It was necessary to operate the gas chromatograph oven and detector at relatively low temperatures (<70 °C) to minimize decomposition of the thiocarbonyl complexes.

A chemical separation was found to be a more convenient method of obtaining pure $W(CO)_5(CS)$. Although this method was not used with $Mo(CO)_5(CS)$ or $Cr(CO)_5(CS)$, it would be expected to work equally well with these complexes. This separation sequence involves conversion of the $W(CO)_5(CS)$ in a mixture with $W(CO)_6$ to $Bu_4N[W(CO)_4(CS)(I)]$ by reaction with $[Bu_4N]I$. The $W(CO)_6$ does not react under the mild conditions employed and may be easily separated from the thiocarbonyl salt. The $Bu_4N[W(CO)_4(CS)(I)]$ is then reconverted in high yields to $W(CO)_5(CS)$ by reaction with Ag^+ and CO (eq 2).

$$[W(CO)_4(CS)(I)]^- + Ag^+ + CO \rightarrow W(CO)_5(CS) + AgI \qquad (2)$$

The $M(CO)_5(CS)$ complexes (M = Cr, W) are quite stable, and contact with air over a period of weeks or months causes very little decomposition. Storage at −20 °C, however, retards a slight darkening of the bright yellow crystals.

Thermal Carbonyl Substitution. In reactions similar to those of the hexacarbonyl analogues, $Cr(CO)_5(CS)$ and $W(CO)_5(CS)$ react with donor ligands at elevated temperatures to yield substituted $M(CO)_4(CS)(L)$ complexes. Thus reactions of $W(CO)_5(CS)$ in refluxing xylene or $Cr(CO)_5(CS)$ in refluxing toluene with PPh_3 give $M(CO)_4(CS)(PPh_3)$. However, in contrast to our previous report[1] that these products are the trans isomers, we now know that they are mixtures of the trans isomers with significant amounts of the *cis*-$M(CO)_4(CS)(PPh_3)$ derivatives (eq 3). These isomers were not

$$M(CO)_5(CS) + PPh_3 \xrightarrow{-CO} \textit{trans}\text{-}M(CO)_4(CS)(PPh_3) + \textit{cis}\text{-}M(CO)_4(CS)(PPh_3) \qquad (3)$$

separable by column chromatography or fractional crystallization. Nevertheless, the pure isomer, *trans*-$W(CO)_4(CS)(PPh_3)$, was obtained by another synthetic route (see below).

Reactions performed in the presence of excess phosphine and allowed to continue after the first substitution had been completed showed ir spectroscopic evidence for the formation of small amounts of $M(CO)_3(CS)(PPh_3)_2$ complexes. However, the major products observed in the ir spectra were $M(CO)_5(PPh_3)$ and $M(CO)_4(PPh_3)_2$. Obviously some loss of CS is occurring on extended reaction.

The *trans*-$W(CO)_4(CS)(py)$ (py = pyridine) complex is the only thiocarbonyl product observed in the reaction of $W(CO)_5(CS)$ with pyridine in xylene at 135 °C (eq 4); no cis

$$W(CO)_5(CS) + py \xrightarrow{-CO} \textit{trans}\text{-}W(CO)_4(CS)(py) \qquad (4)$$

isomer could be detected by ir spectroscopy. Quite large amounts of $W(CO)_5(py)$ are also produced after the initial stage of the reaction, even though no $W(CO)_6$ is present. Unlike $W(CO)_5(CS)$ and $W(CO)_4(CS)(PPh_3)$, which could not be separated from their carbonyl analogues by column chromatography, $W(CO)_4(CS)(py)$ and $W(CO)_5(py)$ did separate on a column.

Attempts to prepare $W(CO)_4(CS)(L)$, where L = PPh_3 or py, by Hg-lamp ultraviolet irradiation gave only very low yields of the products; as contrasted with $M(CO)_6$,[7] the photochemical substitution method is not practical for $W(CO)_5(CS)$.

The thermal reaction of $W(CO)_5(CS)$ with 2,2'-bipyridine surprisingly yielded no thiocarbonyl-containing products, and only $W(CO)_4(bpy)$ was produced. The *o*-phenanthroline ligand gave similar results.

The bidentate ethylenebis(diphenylphosphine) (diphos) ligand, however, reacts with $W(CO)_5(CS)$ at 130 °C or $Cr(CO)_5(CS)$ at 110 °C in xylene to yield $M(CO)_3(CS)(diphos)$ complexes (eq 5). A *mer* geometry is tentatively

$$M(CO)_5(CS) + \text{diphos} \xrightarrow{-2CO} M(CO)_3(CS)(\text{diphos}) \qquad (5)$$

assigned to these complexes since only two infrared ν(CO) bands are observed, and one is a weak, high-frequency band characteristic of an A_1 mode involving two nearly trans carbonyls. The third band expected for this structure is presumably hidden under the strong, lower frequency absorption. No $M(CO)_4(diphos)$ is detected in these preparations, even after extended reaction times with excess ligand. The $M(CO)_4(CS)(diphos)$ intermediates, bearing monodentate diphos, in these reactions were identified by the similarity of their ir spectra to those of the $M(CO)_4(CS)(PPh_3)$ complexes. An analogous reaction between $W(CO)_5(CS)$ and *o*-phenylenebis(dimethylarsine) (diars) gave large amounts of the $W(CO)_4(CS)(diars)$ complex, and closing of the chelate ring was accomplished only by extended heating. The assignment of a *mer* geometry to the $W(CO)_3(CS)(diars)$ product is supported by its ^{13}C NMR spectrum.

Further substitution with the diphos ligand was possible for the tungsten complex. A mixture of $W(CO)_3(CS)(diphos)$ and equimolar diphos, when melted at 195 °C, evolves CO and soon solidifies on formation of the tetrasubstituted $W(CO)(CS)(diphos)_2$ (eq 6). Products resulting from the

$$W(CO)_3(CS)(\text{diphos}) + \text{diphos} \xrightarrow{-2CO} W(CO)(CS)(\text{diphos})_2 \qquad (6)$$

loss of CS could not be detected. The structure of this complex is presumed to have the CO and CS groups mutually cis, based on the geometries of the $W(CO)_3(CS)(diphos)$ precursor and the $W(CO)_2(diphos)_2$ analogue.[8] A similar reaction was attempted between $Cr(CO)_3(CS)(diphos)$ and diphos, but no further substitution was detected, perhaps because of steric effects caused by the smaller metal atom.

Tetrahydrofuran solutions of $W(CO)_5(CS)$ and tetrabutylammonium halides react with gas evolution even at room temperature. The products of these reactions were determined to be exclusively $Bu_4N[$*trans*-$W(CO)_4(CS)(X)]$ (X = Cl, Br, I). Remarkably, the reaction of *trans*-$W(CO)_4(^{13}CO)(CS)$ with the halides showed that there is a very high, if not complete, preference for loss of the trans carbonyl in this substitution process (eq 7).[4]

$$\textit{trans}\text{-}W(CO)_4(^{13}CO)(CS) + X^- \rightarrow [\textit{trans}\text{-}W(CO)_4(CS)(X)]^- + {}^{13}CO \qquad (7)$$

Several attempts were made to substitute a carbonyl group in $[$*trans*-$W(CO)_4(CS)(I)]^-$ by PPh_3. At temperatures of about 100 °C in dioxane, carbonyl substitution was observed, but halide substitution (yielding $W(CO)_4(CS)(PPh_3)$) also occurred. However, the use of $P(4\text{-}ClC_6H_4)_3$ instead of PPh_3 led to the production of mainly $[$*mer*-$W(CO)_3(CS)(I)[P(4\text{-}ClC_6H_4)_3]^-$. This product was not isolated but was characterized by its ir spectrum and its reaction in situ (see below).

Substitution by Halide Abstraction. The abstraction of a halide ion from group 6 $[M(CO)_5(X)]^-$ complexes to produce $M(CO)_5(L)$ products has been effected by $[Et_3O]BF_4$, Ag^+, and $AlCl_3$.[9] Thus it was expected that the $[M(CO)_4(CS)(X)]^-$ complexes might also undergo halide abstraction and subsequent ligand addition. As previously reported,[3] Et_3O^+ was found to react with $[W(CO)_4(CS)(I)]^-$, but much of the product was $IW(CO)_4(CSEt)$, resulting from alkylation of the sulfur. However, addition of Ag^+ to solutions of $[W(CO)_4(CS)(I)]^-$ followed by addition of a ligand gives good yields of $W(CO)_4(CS)(L)$ complexes. Moreover, all of the complexes thus formed are observed to have exclusively trans geometries (eq 8). As previously discussed,[4] the retention of

$$[\textit{trans}\text{-}W(CO)_4(CS)(I)]^- + Ag^+ + L \rightarrow \textit{trans}\text{-}W(CO)_4(CS)(L) + AgI \qquad (8)$$

geometry by the $W(CO)_4(CS)$ moiety in these reactions may be favored by both kinetic and thermodynamic effects. Thus, addition of PPh_3 to an acetone solution of $W(CO)_4(CS)(acetone)$, obtained by iodide abstraction, yields only *trans*-$W(CO)_4(CS)(PPh_3)$. This contrasts with the thermal preparation, which yields a mixture of the cis and trans isomers. Heating a toluene solution of *trans*-$W(CO)_4(CS)(PPh_3)$ to 105 °C for a few minutes yields an identical mixture of isomers.

Reaction of the $W(CO)_4(CS)(acetone)$ intermediate with 2,2'-bipyridine leads directly to *mer*-$W(CO)_3(CS)(bpy)$; a $W(CO)_4(CS)(bpy)$ intermediate could not be detected.

The reaction of $Bu_4N[$*mer*-$W(CO)_3(CS)(I)[P(4\text{-}ClC_6H_4]_3]]$ in dioxane solution (prepared as described above) with Ag^+ and CO yielded largely *cis*-$W(CO)_4(CS)[P(4\text{-}ClC_6H_4)_3]$. Heating a toluene solution of this product to 105 °C for a few minutes gives a mixture of isomers containing largely the trans complex.

Kinetics of Carbonyl Substitution in $W(CO)_5(CS)$. Kinetic studies were carried out on two substitution reactions of $W(CO)_5(CS)$ to gain quantitative information about the reactivity of this complex as compared to that of $W(CO)_6$. The reaction between $W(CO)_5(CS)$ and PPh_3 in decalin was followed from 120.0 to 146.0 °C (Table I). Plots of k_{obsd} vs. $[PPh_3]$ gave intercepts and slopes corresponding to rate

Table I. Kinetic Data[a] for the Reaction of $W(CO)_5(CS)$ with PPh_3 in Decalin Solvent

$10^2[PPh_3]$, M	10^4k_{obsd}, s^{-1}	$10^2[PPh_3]$, M	10^4k_{obsd}, s^{-1}
120.0 °C			
2.302	1.39	6.164	1.74
3.031	1.45	7.649	1.83
3.863	1.54	9.569	2.10
4.626	1.63	11.47	2.19
5.733	1.68		
$k_1 = 1.17 \times 10^{-4}\ s^{-1}$; $k_2 = 8.70 \times 10^{-4}\ M^{-1}\ s^{-1}$			
135.0 °C			
2.882	6.38	7.695	7.75
3.844	6.68	9.542	8.22
4.889	7.02	11.50	8.90
5.733	7.26		
$k_1 = 5.60 \times 10^{-4}\ s^{-1}$; $k_2 = 2.91 \times 10^{-3}\ M^{-1}\ s^{-1}$			
146.0 °C			
3.885	18.1	7.687	20.5
5.771	19.1	9.584	21.7
5.771	19.2	11.54	23.0
$k_1 = 1.54 \times 10^{-3}\ s^{-1}$; $k_2 = 6.30 \times 10^{-3}\ M^{-1}\ s^{-1}$			

[a] $\Delta H_1^* = 31.5 \pm 1$ kcal/mol; $\Delta S_1^* = 3.1 \pm 3$ cal/(deg mol). $\Delta H_2^* = 24.0 \pm 1$ kcal/mol; $\Delta S_2^* = -12.0 \pm 3$ cal/(deg mol).

Table II. Kinetic Data[a] for the Reaction of $W(CO)_5(CS)$ with Bu_4NI in Chlorobenzene Solvent

$10^2[I^-]$, M	10^4k_{obsd}, s^{-1}	$10^2[I^-]$, M	10^4k_{obsd}, s^{-1}
38.2 °C			
3.604	2.34	6.821	4.24
4.412	2.86	8.211	5.10
5.420	3.39	10.49	6.45
$k_2 = 5.87 \times 10^{-3}\ M^{-1}\ s^{-1}$			
48.2 °C			
2.694	4.81	8.146	10.3
3.252	5.60	10.80	17.2
5.407	8.93		
$k_2 = 1.53 \times 10^{-2}\ M^{-1}\ s^{-1}$			
58.2 °C			
3.285	14.8	6.802	29.2
4.369	19.1	8.179	34.2
5.431	23.4		
$k_2 = 4.05 \times 10^{-2}\ M^{-1}\ s^{-1}$			

[a] $\Delta H_2^* = 19.0 \pm 1$ kcal/mol; $\Delta S_2^* = -8.0 \pm 3$ cal/(deg mol).

constants for the (SN1) phosphine-independent (eq 9) and

$$W(CO)_5(CS) \xrightarrow{k_1} W(CO)_4(CS) + CO \xrightarrow[\text{fast}]{PPh_3} W(CO)_4(CS)(PPh_3) \qquad (9)$$

(SN2) phosphine-dependent (eq 10) reactions. Activation

$$W(CO)_5(CS) \xrightarrow{k_2[PPh_3]} W(CO)_4(CS)(PPh_3) + CO \qquad (10)$$

parameters (Table I) were determined for both reactions. The reaction (eq 7) between $W(CO)_5(CS)$ and $[Bu_4N]I$ in chlorobenzene was studied from 38.2 to 58.2 °C (Table II). Plots of k_{obsd} vs. $[I^-]$ show that this reaction is an associative process.

Discussion

Compounds of the type $W(CO)_4(CS)(L)$ can exist in cis and trans forms, which statistically should be present in an equilibrium mixture in a ratio of 4:1. Both *trans*-$W(CO)_4(CS)(PPh_3)$ and *cis*-$W(CO)_4(CS)[P(4\text{-}ClC_6H_4)_3]$ revert upon heating to cis–trans mixtures containing more of the trans isomer. Analysis by ^{13}C NMR spectrometry of equilibrium mixtures of other $W(CO)_4(CS)(L)$ compounds (L = phosphine, phosphite, isocyanide) shows that the cis:trans ratio is always considerably less than 4.[10] The preference of these compounds for a trans geometry in an equilibrium situation could be caused by an anisotropic electronic effect transmitted through the metal or possibly a steric difference between CS and CO. The origin of an electronic effect may be the greater π-acceptor capability of CS as compared to CO.[5] Thus an arrangement with a poorly π-bonding ligand L trans to CS represents a more stable situation than a *cis*-$W(CO)_4(CS)(L)$ structure, which requires that CO (a better π acceptor than L) compete with CS for the π electrons in the two d orbitals which they share. The greater π-acceptor ability of CS as compared to that of CO also suggests that the CO groups in $M(CO)_5(CS)$ will be less strongly bound than in the analogous $M(CO)_6$ complexes. In particular, the carbonyl trans to the CS ligand should be most strongly affected.

It is evident from the conditions necessary to effect carbonyl substitution in the $M(CO)_5(CS)$ complexes and from results of kinetic investigations of these reactions that the thiocarbonyl ligand has indeed activated the complexes toward carbonyl substitution. Eyring plots for $W(CO)_5(CS)$ carbonyl substitution by PPh_3, when extrapolated to 165.7 °C, give dissociative and associative rate constants of $k_1 = 8.26 \times 10^{-3}$ s^{-1} and $k_2 = 2.39 \times 10^{-2}\ M^{-1}\ s^{-1}$. These values compare with $k_1 = 1.1 \times 10^{-4}\ s^{-1}$ and $k_2 = 8.9 \times 10^{-5}\ M^{-1}\ s^{-1}$ for the reaction of $W(CO)_6$ and PPh_3 under the same conditions.[11] These values show that the dissociative (k_1) pathway is approximately 75 times faster in $W(CO)_5(CS)$, while the associative (k_2) route is about 250 times faster.

Similarly, extrapolation of the Eyring plot for the (associative) reaction of $W(CO)_5(CS)$ with I^- up to the temperature (120.0 °C) where the analogous $W(CO)_6$ reaction was studied[12] shows that $W(CO)_5(CS)$ reacts more than 1000 times faster with I^- than does $W(CO)_6$ at this temperature ($4.7\ M^{-1}\ s^{-1}$ as compared to $3.2 \times 10^{-3}\ M^{-1}\ s^{-1}$).

Only one other kinetic study of ligand substitution in a thiocarbonyl complex has been reported. It was found that replacement of *cis*-cyclooctene in $(C_5H_5)Mn(CO)(CS)(C_8H_{14})$ by PPh_3 in methylcyclohexane,[13] a dissociative process, was only about 4 times faster than the analogous reaction of $(C_5H_5)Mn(CO)_2(C_8H_{14})$.[14] The presence of the electron-releasing cyclopentadienyl ligand in this complex may lower the activating effect of the CS ligand toward π-bonding ligand dissociation, and the dissociating olefin may not be as sensitive to the influence of the CS. It should also be noted that in this case the ligand is lost from a position cis to the CS ligand. Thus, part of the large rate acceleration observed for first-order carbonyl loss from $W(CO)_5(CS)$ may be due to its position trans to the CS group.

A high preference for trans dissociation over cis dissociation in $W(CO)_5(CS)$ is indeed observed in gas-phase ligand-exchange studies with labeled ^{13}CO.[4] The trans carbonyl exchanges at least 20 times faster than a cis carbonyl. Substantial trans CO dissociation in $W(CO)_5(CS)^+$ has also been observed in mass spectrometric studies of *trans*-$W(CO)_4(^{13}CO)(CS)$.[15] With an electron beam energy of 70 eV, the labeled carbonyl is lost to form more than twice as much unlabeled $W(CO)_4(CS)^+$ as predicted on a statistical basis.

The trans carbonyl has also been found to be lost with high specificity in the SN2 reaction (eq 7) of *trans*-$W(CO)_4(^{13}CO)(CS)$ with $[Bu_4N]I$.[4] This substitution proceeds at a sufficiently low temperature that isomerization is negligible prior to reaction with the iodide ion. The mechanism of this substitution could involve attack by I^- at the metal atom, accompanied by dissociation of the trans, weakly coordinated CO. The strong π-bonding ability of the CS may promote I^- attack trans to the CS to yield the observed [*trans*-$W(CO)_4(CS)(I)]^-$ product. Alternatively the I^- may attack at the C atom of the trans CO, which would be the most electron-deficient CO group in the molecule. Subsequent rearrangement and loss of the trans CO would give the product. These possibilities cannot be distinguished on the basis of our results.

Conclusions

Kinetic and product studies of substitution reactions reported here have shown that the thiocarbonyl ligand is quite different from the carbonyl ligand in these group 6 complexes. The differences are consistent with a greater π-bonding capacity of the CS ligand as compared to that of CO. Relative to the hexacarbonyl analogue, $W(CO)_5(CS)$ is activated toward CO substitution through both S_N1 and S_N2 pathways. The CS group is thus a labilizing ligand, although it contrasts with other labilizing ligands,[16] which are non π bonding or very weakly π bonding and appear to labilize cis carbonyls.[17] It is tentatively concluded that the labilizing effect of the CS ligand is transmitted largely to the trans CO group, although the cis carbonyls also may be labilized to some extent.

Experimental Section

Methods and Materials. All reactions were performed under an atmosphere of dry, prepurified N_2. Dioxane was distilled from CaH_2 and tetrahydrofuran (THF) was distilled from lithium aluminum hydride before use. Elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz., or Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.

Gas chromatographic analyses were performed using a 0.25-in. × 5 ft 2% SE-30 column at 60–150 °C and a helium flow rate of 25 cm^3/min. The same column was used for preparative collections of $Cr(CO)_5(CS)$ and $W(CO)_5(CS)$ at 55–65 °C and a helium flow rate of 100 cm^3/min. Approximately 45 μl of a saturated pentane or hexane solution was injected for each preparative collection.

Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrometer. Positions of the peaks were determined with an expanded-scale recorder calibrated in the carbonyl region with gaseous CO and DCl and in the thiocarbonyl region with polystyrene. Proton NMR spectra were recorded with Varian A-60 and Perkin-Elmer Hitachi R-20B instruments. ^{13}C NMR spectra were obtained with a Bruker HX-90 spectrometer operating in the Fourier transform mode. Samples were run in $DCCl_3$ containing 0.05 M $Cr(acac)_3$, a shiftless relaxation reagent.[18]

Solvents and reagents used in kinetic experiments were carefully purified before use. Decalin was stirred overnight with Na at 130 °C and fractionally distilled under reduced pressure onto molecular sieves. Chlorobenzene was distilled from P_4O_{10} and stored over molecular sieves. Triphenylphosphine was recrystallized twice from hexane and dried under high vacuum. Tetra-*n*-butylammonium iodide was recrystallized twice from chlorobenzene, powdered, and dried under high vacuum. Kinetic experiments were performed in flasks capped with rubber serum stoppers under N_2, from which samples were periodically withdrawn by syringe. Experiments above 100 °C were carried out in 10-ml syringes to prevent sublimation of the complexes.[11] The reaction vessels were immersed in a constant-temperature oil bath (±0.05 °C). Substitution reactions were carried out with at least a tenfold excess of the ligand. Rates of these reactions were determined by following the disappearance of the 2096-cm^{-1} ir band of $W(CO)_5(CS)$. Plots of $\ln (A - A_\infty)$ vs. t were linear with slopes of $-k_{obsd}$, confirming pseudo-first-order kinetics. The average deviation of rate constants for identical reactions was less than 5%.

Preparation of $Cr(CO)_5(CS)$. A solution of $Cr(CO)_6$ (20.0 g, 91 mmol) in 200 ml of tetrahydrofuran (THF) was refluxed and stirred mechanically in a 1000-ml three-necked flask with excess sodium amalgam (4.0 g of Na, 173 mmol, and 40 ml of Hg). After 12 h the solution was cooled to 25 °C and decanted under N_2 from the amalgam into an addition funnel. This solution was then added over a 5-min period to Cl_2CS (9.0 ml, 117 mmol) in 75 ml of THF with rapid stirring. The mixture was stirred until it had cooled to room temperature and was then evaporated to dryness under water-aspirator vacuum on a rotary evaporator. Sublimation of the residue at 55 °C under high vacuum onto a water-cooled probe yielded 6.5 g of a mixture of $Cr(CO)_5(CS)$ and $Cr(CO)_6$. Gas chromatographic analysis of the mixture indicated that 0.9 g of $Cr(CO)_5(CS)$ had been produced (4.2% based on $Cr(CO)_6$). A combined mixture of $Cr(CO)_5(CS)$ (3 g) and $Cr(CO)_6$ (17 g) obtained from several preparative reactions was dissolved in 700 ml of refluxing pentane. The flask containing the solution was stoppered and placed in warm water in a covered Dewar flask. This bath was then placed in a refrigerator at 0 °C and allowed to cool slowly for 2 days. The solution, which is enriched in $Cr(CO)_5(CS)$, was decanted from the crystals, which contained a high proportion of $Cr(CO)_6$. The solution was concentrated with warming and then cooled slowly as before. After four crystallizations the solution was found by gas chromatography to contain less than 1% $Cr(CO)_6$. It was passed through a Florisil/pentane column, evaporated to dryness, and sublimed under high vacuum to yield 0.6 g of $Cr(CO)_5(CS)$. Ir (hexane): 2091 (w), 2023 (m), 1997 (vs), and ν(CS) in CS_2 at 1253 (vs) cm^{-1}. ^{13}C NMR ($DCCl_3$): $\delta(^{13}CO)$ at −211.4 ppm (cis and trans); $\delta(^{13}CS)$ at −331.1 ppm. The mass spectrum showed the parent ion at m/e 236.

Anal. Calcd for $Cr(CO)_5(CS)$: C, 30.51; H, 0.00; S, 13.56. Found: C, 30.14; H, <0.01; S, 13.59.

Preparation of $Mo(CO)_5(CS)$. Molybdenum hexacarbonyl (20.0 g, 76 mmol) was stirred with excess sodium amalgam in 350 ml of refluxing THF for 12 h. Twenty-milliliter quantities of the THF solution (2.2 mequiv) at room temperature were withdrawn by syringe and added to a solution of Cl_2CS (0.35 ml, 4.8 mmol) in 3 ml of THF with stirring. Each small reaction mixture was evaporated to dryness and sublimed individually. Infrared spectra of the products indicated yields of $Mo(CO)_5(CS)$ in the range of 2–4%. The use of larger quantities of starting materials reduced the yields; increasing the quantities by a factor of 4 gave no $Mo(CO)_5(CS)$. The combined sublimates from many small reactions were dissolved in warm pentane and allowed to cool to 0 °C over several hours. The solution was decanted from the crystals, concentrated, warmed, and crystallized in this manner twice more. Evaporation of the pentane solvent gave a small quantity of a mixture containing approximately 75% $Mo(CO)_5(CS)$. Ir (hexane): 2096 (w), 2020 (m), 1995 (vs), and ν(CS) in CS_2 at 1247 (vs) cm^{-1}. The mass spectrum showed the parent ion at m/e 280.

Preparation of $W(CO)_5(CS)$. A solution of $W(CO)_6$ (50 g, 142 mmol) in 400 ml of THF was mechanically stirred with excess sodium amalgam (7.0 g of Na, 304 mmol, and 120 ml of Hg) and refluxed for 12 h. The mixture was allowed to cool to room temperature and was decanted from the amalgam into an addition funnel under N_2. It was then added over a 5-min period, with stirring, to Cl_2CS (14 ml, 183 mmol) in 100 ml of THF in a 1000-ml round-bottom flask. After cooling to room temperature, the mixture was evaporated to dryness on a rotary evaporator under a water-aspirator vacuum. Sublimation at 20 Torr and 65 °C onto a water-cooled probe gave yellow crystals (14 g) which were found by gas chromatography to contain 6.3 g of $W(CO)_5(CS)$ (12% yield based on $W(CO)_6$). The complex was purified by repeated crystallization (five times) of a hexane solution of the mixture, as outlined for $Cr(CO)_5(CS)$, to yield 1.5 g of 99% $W(CO)_5(CS)$. Ir (hexane): 2096 (w), 2007 (m), 1989 (vs), and ν(CS) in CS_2 at 1258 (vs) cm^{-1}. ^{13}C NMR ($DCCl_3$): $\delta(^{13}CO)$ at −192.4 ppm (cis) and −189.3 ppm (trans); $\delta(^{13}CS)$ at −298.7 ppm. The mass spectrum showed the parent ion at m/e 368.

Anal. Calcd for $W(CO)_5(CS)$: C, 19.55; H, 0.00; S, 8.70. Found: C, 18.93; H, <0.01; S, 8.36.

Preparation of $W(CO)_4(CS)(PPh_3)$. A xylene solution (15 ml) of $W(CO)_5(CS)$ (0.20 g, 0.54 mmol) and PPh_3 (0.14 g, 0.54 mmol) was heated near reflux for 20 min. At this time the ir spectrum indicated nearly complete consumption of the $W(CO)_5(CS)$, so the mixture was immediately cooled and placed on a 1.5 × 40 cm Florisil/pentane column. After washing of the column well with pentane, a 2:1 pentane–benzene eluent was used until the yellow band had moved from the top. The top 5 cm of the column was mechanically removed, and development was accomplished with CH_2Cl_2. The yellow band was collected, the solution was concentrated, hexane was added, and concentration was continued until crystallization began. Cooling to −20 °C gave 0.14 g of yellow crystals (42%). The mixture of *cis*- and *trans*-$W(CO)_4(CS)(PPh_3)$ was recrystallized from hexane. Ir (hexane): 2061 (vvw) (trans), 2052 (w) (cis), 1981 (w) (cis), 1956 (vs) (cis and trans), and ν(CS) in CS_2 at 1241 (vs) (cis and trans) cm^{-1}. ^1H NMR ($DCCl_3$): τ 2.75 m. The mass spectrum showed the parent ion at m/e 602.

Anal. Calcd for $W(CO)_4(CS)(PPh_3)$: C, 45.8; H, 2.49; S, 5.32. Found: C, 46.15; H, 2.50; S, 5.11.

Preparation of $Cr(CO)_4(CS)(PPh_3)$. A toluene solution (5 ml) of $Cr(CO)_5(CS)$ (0.32 g, 1.45 mmol) and PPh_3 (0.40 g, 1.52 mmol) was refluxed for 15 min, and the progress of the reaction was followed by ir spectroscopy. The mixture was cooled and placed on a 1.5 × 40 cm Florisil/hexane column. After washing with hexane, the column was developed with 1:1 hexane/CH_2Cl_2 and the yellow $Cr(CO)_4(CS)(PPh_3)$ band was collected. Concentration and cooling of the solution to −20 °C gave 0.20 g of yellow crystals (34%). The product mixture of *cis*- and *trans*-$Cr(CO)_4(CS)(PPh_3)$ was recrystallized from 1:1 hexane/CH_2Cl_2. Ir (hexane): 2063 (vvw) (trans), 2044 (w) (cis), 1992 (vw) (cis), 1960 (vs) (cis and trans), and ν(CS) in CS_2 at 1230 (s) (cis and trans) cm^{-1}. ^1H NMR ($DCCl_3$): τ 2.77 m. The mass spectrum showed the parent ion at *m/e* 470.

Anal. Calcd for $Cr(CO)_4(CS)(PPh_3)$: C, 58.7; H, 3.19; S, 6.80. Found: C, 59.11; H, 3.24; S, 6.01.

Preparation of *trans*-$W(CO)_4(CS)(NC_5H_5)$. A mixture containing 1.5 g (4.1 mmol) of $W(CO)_5(CS)$ and 1.0 g of $W(CO)_6$ was refluxed in 10 ml of xylene with pyridine (2.5 ml, 31 mmol) for 5 min. At this time, the amount of remaining $W(CO)_5(CS)$ was still quite large, but $W(CO)_5(py)$ began to appear, so the reaction was stopped. The mixture was poured onto a 1.5 × 35 cm Florisil/hexane column and washed with hexane. Development with benzene brought down a broad yellow band, the front of which was $W(CO)_5(py)$. The latter portion of the band was quite pure *trans*-$W(CO)_4(CS)(py)$, which was collected and evaporated to dryness. Crystallization from pentane gave 0.17 g (10%) of the product. Ir (hexane): 2062 (vw), 1950 (vs), and ν(CS) in CS_2 at 1224 (vs) cm^{-1}. ^1H NMR ($DCCl_3$): τ 1.5 (2 H) m, 2.3 (1 H) m, 2.7 (2 H) m. The mass spectrum showed the parent ion at *m/e* 419.

Anal. Calcd for $W(CO)_4(CS)(NC_5H_5)$: C, 28.6; H, 1.19; S, 7.64. Found: C, 28.83; H, 1.18; S, 7.38.

Preparation of $W(CO)_3(CS)$(diphos). A mixture of $W(CO)_5(CS)$ and $W(CO)_6$ containing 1.5 g of $W(CO)_5(CS)$ (4.1 mmol) was dissolved in 50 ml of xylene with diphos (2.0 g, 5.0 mmol). The solution was heated to 132 °C for 1 h and then cooled and evaporated to dryness under vacuum. The residue was dissolved in 100 ml of CH_2Cl_2 and the solution was filtered. Approximately 80 ml of pentane was added with warming, and crystallization was accomplished by cooling to −20 °C. Yellow flakes of the product (2.55 g, 88%) were collected and recrystallized from CH_2Cl_2/hexane. Ir (CH_2Cl_2): 2013 (w), 1925 (vs), and ν(CS) in CS_2 at 1215 (s) cm^{-1}. ^1H NMR ($DCCl_3$): τ 2.6 m, 7.42 m. The mass spectrum showed the parent ion at *m/e* 710.

Anal. Calcd for $W(CO)_3(CS)$(diphos): C, 50.7; H, 3.38. Found: C, 49.0; H, 3.48.

Preparation of $Cr(CO)_3(CS)$(diphos). A xylene solution (10 ml) of $Cr(CO)_5(CS)$ (0.17 g, 0.77 mmol) and diphos (0.32 g, 0.80 mmol) was heated to 110 °C for approximately 1 h, and the reaction was followed by ir spectroscopy. Substantial amounts of $Cr(CO)_4(CS)$(diphos) formed in the initial stages of the reaction, and continued heating was necessary to allow the second phosphorus atom to coordinate. After evaporation of the solvent, the residue was dissolved in 15 ml of CH_2Cl_2, the solution was filtered, and crystallization was effected by addition of pentane and cooling to −20 °C. Yellow-orange crystals of the product (0.31 g, 75%) were collected and recrystallized from CH_2Cl_2/hexane. Ir (CS_2): 2006 (w), 1924 (vs), and ν(CS) at 1209 (vs) cm^{-1}. The mass spectrum showed the parent ion at *m/e* 578.

Anal. Calcd for $Cr(CO)_3(CS)$(diphos): C, 62.2; H, 4.15; S, 5.53. Found: C, 61.1; H, 4.29; S, 5.05.

Preparation of $W(CO)_3(CS)$(diars). A solution of $W(CO)_5(CS)$ (1.0 g, 2.7 mmol) and *o*-phenylenebis(dimethylarsine), diars (0.84 g, 2.9 mmol), in 5 ml of xylene was heated to 140 °C under a stream of N_2. In the early stages of the reaction only a monosubstituted complex was seen in the ir spectrum (2070 (w), 1940 (vs) cm^{-1}, in hexane). However, after 2.5 h, mainly $W(CO)_3(CS)$(diars) had formed. The solution was cooled and poured onto a 2 × 35 cm Florisil/hexane column under N_2. The yellow band was eluted with CH_2Cl_2, collected, concentrated, and crystallized by the addition of pentane with cooling to −20 °C (1.2 g, 78%). The complex was recrystallized from hexane. Ir (hexane): 2010 (w), 1928 (m), 1919 (vs), and ν(CS) in CS_2 at 1213 (s) cm^{-1}. ^{13}C NMR ($DCCl_3$): $\delta(^{13}CO)$ at −210.2 ppm (1 C) and −201.9 ppm (2 C); $\delta(^{13}CS)$ at −306.9 ppm. The mass spectrum showed the parent ion at *m/e* 568.

Anal. Calcd for $W(CO)_3(CS)$(diars): C, 28.09; H, 2.68. Found: C, 27.26; H, 2.55.

Preparation of $W(CO)(CS)(diphos)_2$. A 5-ml flask containing a mixture of $W(CO)_3(CS)$(diphos) (4.70 g, 6.6 mmol) and diphos (2.70 g, 6.8 mmol) was evacuated on a vacuum line and filled with N_2 at atmospheric pressure. After connection of it to a nitrogen bubbler, the flask was heated to 195 °C. After approximately 30 min the molten mixture solidified, but heating was continued for a total of 1 hr. The solid was cooled to room temperature and slurried in 15 ml of CH_2Cl_2. The mixture was then filtered, leaving a bright yellow powder on the filter. This was washed with 15 ml of CH_2Cl_2 and dried to yield 6.92 g (99%) of quite pure $W(CO)(CS)(diphos)_2$. A small sample of the product was recrystallized by repeatedly extracting with hot CS_2, filtering the solution, and crystallizing at −20 °C. Ir (CH_2Cl_2): 1838 (s) and ν(CS) at 1161 (s) cm^{-1}.

Anal. Calcd for $W(CO)(CS)(diphos)_2$: C, 61.59; H, 4.56. Found: C, 61.29; H, 4.85.

Preparation of Bu_4N[*trans*-$W(CO)_4(CS)(I)$]. A solution of $W(CO)_5(CS)$ (0.15 g, 0.41 mmol) and $[Bu_4N]I$ (0.15 g, 0.41 mmol) in 15 ml of THF was stirred at 35 °C for 1.5 h. The THF solution was then concentrated to about 10 ml, and 20 ml of a mixture of hexane and ethyl ether was added. Cooling to −20 °C gave 0.23 g of yellow crystals. A second crop of 0.03 g was also collected, for a total yield of 90%. The product was recrystallized from CH_2Cl_2/ethyl ether. Ir (CH_2Cl_2): 2062 (w), 1947 (vs), and ν(CS) at 1195 (vs) cm^{-1}. Molar conductivity (10^{-3} M in nitrobenzene): $\Lambda = 25.6\ ohm^{-1}\ cm^2\ mol^{-1}$. ^{13}C NMR ($DCCl_3$): $\delta(^{13}CO)$ at −196.5 ppm ($J_{^{183}W-^{13}C} = 128$ Hz) and $\delta(^{13}CS)$ at −285.7 ppm.

Anal. Calcd for $Bu_4N[IW(CO)_4(CS)]$: C, 35.54; H, 5.08; S, 4.52. Found: C, 35.05; H, 5.09; S, 4.67.

This preparation was also commonly performed on a large scale using a mixture of $W(CO)_5(CS)$ and $W(CO)_6$ which does not react under these conditions. For example, a THF solution (125 ml) of a mixture containing 3.3 g of $W(CO)_5(CS)$ (9.0 mmol) and $[Bu_4N]I$ (3.3 g, 9.0 mmol) was stirred at 50 °C for 2 h. The solution was then concentrated to about 20 ml and crystallized by the addition of 30 ml of ethyl ether. The solid was washed well with ether and dried at 50 °C under high vacuum overnight to remove any traces of $W(CO)_6$. A yield of 6.4 g (99%) was collected.

Preparation of Bu_4N[*trans*-$BrW(CO)_4(CS)$]. A THF solution (50 ml) of $[Bu_4N]Br$ (0.45 g, 1.4 mmol) and $W(CO)_5(CS)$ (0.5 g, 1.36 mmol) was heated at 40 °C for 1 h. The mixture was concentrated to 10 ml and diluted with 10 ml of ethyl ether and 10 ml of hexane. Cooling to −20 °C overnight gave 0.5 g of dark yellow crystals (55%). The product was recrystallized from CH_2Cl_2/ether. Ir (CH_2Cl_2): 2065 (w), 1947 (vs), and ν(CS) at 1193 (s) cm^{-1}. ^{13}C NMR ($DCCl_3$): $\delta(^{13}CO)$ at −198.5 ppm and $\delta(^{13}CS)$ at −287.4 ppm.

Anal. Calcd for $Bu_4N[BrW(CO)_4(CS)]$: C, 38.65; H, 5.52. Found: C, 38.10; H, 5.58.

Preparation of Bu_4N[*trans*-$ClW(CO)_4(CS)$]. A THF solution (25 ml) of $W(CO)_5(CS)$ (0.86 g, 2.33 mmol) and $[Bu_4N]Cl$ (0.65 g, 2.34 mmol) was stirred at room temperature for 1.5 h. It was then concentrated to 10 ml and diluted with 10 ml of ethyl ether, which caused the formation of an oil. Cooling to −20 °C solidified the oil, and it was dried under high vacuum. A crude yield of 0.75 g (52%) was collected. The complex was characterized only by its ir and ^{13}C NMR spectra. Ir (CH_2Cl_2): 2064 (w), 1945 (vs), and ν(CS) at 1193 (s) cm^{-1}. ^{13}C NMR ($DCCl_3$): $\delta(^{13}CO)$ at −199.2 ppm and $\delta(^{13}CS)$ at −287.3 ppm.

Preparation of *trans*-$W(CO)_4(CS)(PPh_3)$. A solution of $Bu_4N[IW(CO)_4(CS)]$ (0.20 g, 0.282 mmol) in 5 ml of acetone was stirred under N_2 while silver trifluoromethanesulfonate, $AgCF_3SO_3$ (0.073 g, 0.284 mmol), in 3 ml of acetone was added over a 2-min period. A voluminous yellow precipitate of AgI immediately formed. Triphenylphosphine (0.08 g, 0.305 mmol) in 3 ml of acetone was then added and the solution was stirred for 1.5 h at 25 °C. After filtration through Celite filter aid and evaporation of the solution to dryness, the residue was extracted with 25 ml of warm hexane. The solution was filtered and cooled to −20 °C to yield 0.12 g of yellow crystals. A second crop of 0.02 g was also obtained, for a total yield of 82%. Ir (hexane): 2061 (vvw), 1956 (vs), and ν(CS) in CS_2 at 1247 (vs) cm^{-1}.

Heating a sample of this compound in xylene solution to 105 °C for 10 min caused isomerization to a mixture of isomers identical with that obtained from the thermal preparation.

Preparation of *mer*-$W(CO)_3(CS)$(bpy). A solution of $Bu_4N[IW(CO)_4(CS)]$ (0.20 g, 0.282 mmol) in 15 ml of acetone was stirred under N_2 while $AgCF_3SO_3$ (0.0725 g, 0.282 mmol) in 2 ml of acetone was added dropwise. Then 2,2′-bipyridine (bpy) (0.044 g, 0.282 mmol) was added to the mixture, which caused the immediate formation of a dark red color. The solution was filtered through Celite and evaporated to dryness, and the residue was dissolved in CH_2Cl_2. This solution was placed on a 1.5 × 20 cm Florisil/CH_2Cl_2 column. Elution with CH_2Cl_2 gave a red band which was collected, concentrated, diluted with hexane, and cooled to −20 °C. Dark red crystals (0.075 g, 57%) were collected. Ir (CS_2): 2004 (w), 1916 (vs), 1888 (m), and ν(CS) at 1203 (s) cm^{-1}.

Anal. Calcd for $W(CO)_3(CS)(bpy)$: C, 35.90; H, 1.71. Found: C, 35.24; H, 1.63.

Preparation of $W(CO)_5(CS)$ from $Bu_4N[W(CO)_4(CS)(I)]$. A 250-ml beverage bottle[19] containing $Bu_4N[W(CO)_4(CS)(I)]$ (5.1 g, 7.2 mmol) in 150 ml of acetone was flushed with CO and capped. A solution of $AgCF_3CO_3$ (1.85 g, 7.2 mmol) in 5 ml of acetone was added through a syringe, with stirring, and the bottle was pressured with 30 psi of CO. The mixture was stirred vigorously with a magnetic stirrer for 6 h, with occasional CO repressuring. The solution was then filtered through Celite and evaporated to dryness. The residue was extracted with warm hexane; the solution was then filtered, concentrated, and passed through a 2 × 40 cm Florisil/hexane column. Evaporation under reduced pressure gave 2.15 g (83%) of $W(CO)_5(CS)$.

Reaction of $Bu_4N[W(CO)_4CS)(I)]$ with $P(4\text{-}ClC_6H_4)_3$ and Preparation of *cis*-$W(CO)_4(CS)[P(4\text{-}ClC_6H_4)_3]$. A dioxane solution (10 ml) of $Bu_4N[W(CO)_4(CS)(I)]$ (0.25 g, 0.35 mmol) and $P(4\text{-}ClC_6H_4)_3$ (0.14 g, 0.38 mmol) was stirred at 75 °C while N_2 was bubbled through the solution. After 30 min the ir spectrum showed that most of the starting complex had been converted to a new compound, presumably $Bu_4N[$*mer*-$W(CO)_3(CS)(I)[P(4\text{-}ClC_6H_4)_3]]$, with ν(CO) bands at 2012 (m) and 1914 (vs) and a ν(CS) band at 1175 (m) cm^{-1} in CH_2Cl_2 solvent.

The above solution was cooled to room temperature and saturated with CO while $AgCF_3SO_3$ (0.09 g, 0.35 mmol) in 3 ml of acetone was added dropwise. Stirring and CO saturation were continued for 1.5 h. The solution was then filtered through Celite and evaporated to dryness on a rotary evaporator under reduced pressure. The residue was extracted four times with warm hexane. These extracts were combined, concentrated, and placed on a 1.5 × 30 cm Florisil/hexane column. Development with 1:2 CH_2Cl_2/hexane brought down a yellow band which was concentrated and cooled at −20 °C. Large yellow crystals (0.025 g, 10%) found to be mainly *cis*-$W(CO)_4(CS)[P(4\text{-}ClC_6H_4)_3]$ were collected. Ir (hexane): 2053 (m), 1981 (w), 1963 (m), 1955 (s), and ν(CS) in CS_2 at 1245 (s) cm^{-1}. The mass spectrum showed the parent ion at *m/e* 704.

Anal. Calcd for $W(CO)_4(CS)[P(4\text{-}ClC_6H_4)_3]$: C, 39.12; H, 1.70. Found: C, 40.00; H, 1.72.

Heating a sample of this complex in xylene solution at 105 °C for 10 min caused isomerization to a cis–trans mixture containing mainly the trans isomer, as indicated by the growth of a very strong band at 1956 cm^{-1} in the ir spectrum.

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Registry No. $Cr(CO)_5(CS)$, 50358-90-2; $Mo(CO)_5(CS)$, 50358-91-3; $W(CO)_5(CS)$, 50358-92-4; *cis*-$W(CO)_4(CS)(PPh_3)$, 58617-28-0; *trans*-$W(CO)_4(CS)(PPh_3)$, 50358-94-6; *cis*-$Cr(CO)_4(CS)(PPh_3)$, 58616-82-3; *trans*-$Cr(CO)_4(CS)(PPh_3)$, 50358-93-5; *trans*-$W(CO)_4(CS)(NC_5H_5)$, 50358-95-7; *mer*-$W(CO)_3(CS)$(diphos), 54204-88-5; *mer*-$Cr(CO)_3(CS)$(diphos), 58569-40-7; *mer*-$W(CO)_3(CS)$(diars), 58569-41-8; *cis*-$W(CO)(CS)(diphos)_2$, 54203-47-3; $Bu_4N[$*trans*-$W(CO)_4(CS)(I)]$, 56031-00-6; $Bu_4N[$*trans*-$BrW(CO)_4(CS)]$, 58569-43-0; $Bu_4N[$*trans*-$ClW(CO)_4(CS)]$, 58569-45-2; *mer*-$W(CO)_3(CS)$(bpy), 58569-46-3; $Bu_4N[W(CO)_3(CS)(I)[P(4\text{-}ClC_6H_4)_3]]$, 58569-48-5; *cis*-$W(CO)_4(CS)[P(4\text{-}ClC_6H_4)_3]$, 58569-49-6; *trans*-$W(CO)_4(CS)[P(4\text{-}ClC_6H_4)_3]$, 58616-83-4; PPh_3, 603-35-0; Bu_4NI, 311-28-4; py, 110-86-1; bpy, 366-18-7; Cl_2CS, 463-71-8.

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