pure *trans*-$Mo(CO)_4[P(C_6H_5)_3]_2$, prepared thermally from $Mo(CO)_6$ and triphenylphosphine in diglyme, was found to undergo photochemical isomerization to the cis isomer. However, the trans → cis conversion is not noticeably faster than the net reaction of $Mo(CO)_5P(C_6H_5)_3$ with triphenylphosphine. A definitive explanation will have to await accurate quantum yield studies of the net reaction and the trans → cis isomerization processes.[16]

The reactions of $W(CO)_5P(C_6H_5)_3$ with piperidine and pyridine were observed as a function of the wavelength region irradiated and the irradiation time (Figure 2). Maximum yields were initially (30 min) obtained utilizing irradiation covering the entire visible and uv region (*i.e.*, no filter, 75% transmission at 2000 Å, Figure 1). Although the initial yields are less utilizing a Pyrex filter (zero transmission at $\lambda < 2800$ Å, Figure 1), a yield comparable to that with no filter is obtained after a much longer irradiation time. The lower energy irradiation evidently does not decompose the product as rapidly as the full-wavelength range.

$M(CO)_5L$ compounds have electronic absorption spectra which consist essentially of two intense bands with quite different oscillator strengths. These absorptions occur at approximately 3050 and 2300 Å in the $M(CO)_5P(C_6H_5)_3$ compounds with oscillator strengths of $\sim 0.05$ and $\sim 1.0$, respectively, and at about 4000 and 2500 Å in the $M(CO)_5$(amine) compounds with oscillator strengths comparable to those of the phosphine derivatives. From the magnitude of the oscillator strengths these bands are thought to be charge-transfer bands involving metal-to-ligand and/or ligand-to-metal character.[17] Although we have not obtained quantum yield data involving isolated irradiation of these two principal bands, it is quite apparent that irradiation of either of these bands leads to product formation. This conclusion is further substantiated by irradiation of $W(CO)_5NHC_5H_{10}$ in the presence of $P(C_6H_5)_3$ with light of wavelength $< 5150$ Å to yield 11% of the disubstituted *cis*-$W(CO)_4[P(C_6H_5)_3]NHC_5H_{10}$ product after 2.5-hr irradiation. In this region there is only present the tail absorptions of the lower energy, less intense band at about 4000 Å.

## Conclusions

The preparation of mixed phosphine–amine ligand compounds of molybdenum and tungsten is achieved in good yield from either the metal pentacarbonyl phosphine or amine photolysis reaction. These reactions indicate the sensitivity of the metal–carbon monoxide bond cleavage to both visible and ultraviolet irradiation, whereas the metal–phosphorus and metal–nitrogen bonds are substitution inert. In the case of the metal–nitrogen species this result is contrary to its thermal behavior in which the metal–nitrogen bond is much more labile than the metal–carbon monoxide bond.[11,12]

It has also been suggested that the stereochemistry of the resultant product from photolysis of the group VI substituted metal carbonyl is determined not only by electronic effects but by the size of the central metal atom as well as the spatial requirements of the substituted ligand. For example, photolysis of $Cr(CO)_5P(C_6H_5)_3$ with $P(C_6H_5)_3$ produces *trans*-$Cr(CO)_4[P(C_6H_5)_3]_2$, whereas the analogous reaction of $W(CO)_5P(C_6H_5)_3$ produces *cis*-$W(CO)_4[P(C_6H_5)_3]_2$, and $W(CO)_5[P(C_6H_{11})_3]$ in the presence of $P(C_6H_{11})_3$ forms *trans*-$W(CO)_4[P(C_6H_{11})_3]_2$. In addition the photolysis of $M(CO)_5L$ compounds in the presence of $^{13}CO$ appears to be an excellent procedure for selectively labeling these species, a technique which has had little success thermally.

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# Preparation and Characterization of Several Molybdenum and Tungsten Hexaisothiocyanate Complexes

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Although usually poorly characterized, thiocyanate complexes of molybdenum and tungsten have been known for several years. Oxythiocyanates of tungsten(V)[1] and molybdenum(V)[2] have been prepared. Starting with molybdenum(V) and tungsten(VI) chlorides, Funk and Bohland[3] prepared a number of complexes in which several or all of the chloride ions were replaced by thiocyanate ions, *e.g.*, $Mo(CNS)_5 \cdot 2(CH_3)_2CO$ and $W(CNS)_6 \cdot 2(CH_3)_2CO$. Attempts to remove the solvent were unsuccessful. Lower oxidation state complexes of tungsten and molybdenum have also been prepared, *e.g.*, $W(CO)_5NCS^-$, $Mo(CO)_5NCS^-$,[4] $C_5H_5W(CO)_2CNS$, and $C_5H_5Mo(CO)_2CNS$,[5] and the mode of bonding of the thiocyanate ion has been investigated. Hexathiocyanato complexes of molybdenum(III)[6] have been prepared and were found to be N bonded.[7,8] The hexathiocyanato complex of molybdenum(IV), $(pyH)_2Mo(CNS)_6$,[9,10] has been poorly characterized and the bonding mode is unknown. It has been proposed by Jørgensen[11] that the molybdenum(V) thiocyanato

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TABLE I
ANALYTICAL DATA[a]

| Complex | % Mo or W | % C | % H | % N | % S | Mp, °C | Color |
|---|---|---|---|---|---|---|---|
| $K_2Mo(NCS)_6$ | 18.87 (18.36) | 13.51 (13.79) | | 15.87 (16.08) | 36.35 (36.81) | | Blue-black |
| $[(C_4H_9)_4N]_2[Mo(NCS)_6]$ | | 49.40 (49.11) | 8.09 (7.81) | 11.85 (12.06) | 20.38 (20.70) | ~140 | Black |
| $K_2W(NCS)_6$ | 29.80 (30.11) | 11.90 (11.80) | | 13.61 (13.78) | 31.41 (31.50) | | Dark red |
| $[(C_6H_5)_4As]_2[W(NCS)_6]$[b] | 14.30 (14.14) | 50.16 (49.93) | 3.23 (3.10) | 6.21 (6.47) | 14.52 (14.78) | ~289 | Dark red |
| $KW(NCS)_6$ | 32.41 (32.17) | 12.80 (12.61) | | 14.42 (14.71) | 33.29 (33.67) | | Black |
| $[(C_4H_9)_4N][W(NCS)_6]$ | | 33.96 (34.10) | 4.81 (4.68) | 12.63 (12.65) | 24.68 (24.83) | ~140 | Dark brown |

[a] Calculated values in parentheses. [b] Per cent arsenic: calcd, 11.53; found, 11.26.

TABLE II
SUMMARY OF INFRARED ABSORPTION FREQUENCIES ($CM^{-1}$) FOR COMPLEXES PREPARED IN THIS STUDY

| Compound | Medium[a] | $\nu$(CN)[b] | $\nu$(CS)[b] | $\delta$(NCS)[b] | 2$\delta$(NCS)[b] | $\nu$(MN)[b] |
|---|---|---|---|---|---|---|
| $K_2W(NCS)_6$ | M | 2055 (vs)<br>2015 (vs)<br>1960 (vs) | | 494 (s) | 970 (w) | 281 (vs) |
| | A | 2038 (vs) | | | | |
| $[(C_6H_5)_4As]_2W(NCS)_6$ | M | 2095 (vs)<br>2030 (sh)<br>2005 (vs)<br>1981 (sh) | [c] | 477 (s) | [c] | 267 (vs) |
| $K_2Mo(NCS)_6$ | M | 2080 (vs)<br>2025 (vs)<br>1960 (vs) | | 489 (s) | 975 (w) | 315 (vs) |
| | A | 2065 (vs) | | | | |
| $[(C_4H_9)_4N]_2Mo(NCS)_6$ | M | 2050 (vs)<br>1988 (vs)<br>1969 (vs) | [c] | 481 (s) | [c] | 305 (vs) |
| $KW(NCS)_6$ | M | 2040 (vs)<br>2010 (vs)<br>1992 (vs)<br>1950 (vs)<br>1910 (vs) | | 497 (s) | | 305 (vs) |
| | A | 1980 (vs) | | | | |
| $[(C_4H_9)_4N]W(NCS)_6$ | M | 2020 (vs)<br>1985 (vs)<br>1945 (vs)<br>1920 (vs) | [c] | 490 (s) | [c] | 262 (vs) |

[a] M = Nujol mull; A = acetonitrile. [b] Relative intensities: s, strong; m, medium; w, weak; v, very; sh, shoulder. [c] Region masked by cation absorption.

complexes should be S bonded. In view of the ambiguities in the above results and observations a study of the thiocyanate complexes of molybdenum(IV) and tungsten(IV) and -(V) was made and the results of these investigations are presented here.

## Experimental Section

All reactions were carried out in an inert-atmosphere (nitrogen) box or on a vacuum line. A reaction-extraction vessel used for some of the preparations was similar to that previously reported.[12]

**Materials.**—Molybdenum(V) chloride supplied by Climax Molybdenum Co. was purified by sublimation prior to use. Molybdenum(IV) chloride was obtained from Climax Molybdenum Co. as a gift and was used without purification. Tungsten(VI) chloride was purchased from Research Inorganics and was purified by sublimation prior to use. Tungsten(V) chloride was prepared from tungsten(VI) chloride by the method of Brown and McCann.[13] Tetrachlorobis(acetonitrile)tungsten(IV) was prepared from tungsten(V) chloride or tungsten hexachloride in acetonitrile. The yield was *ca.* 90%, based on $WCl_5$. *Anal.* Calcd for $WCl_4 \cdot 2CH_3CN$: W, 45.09; C, 11.78; H, 1.48; N, 6.87. Found: W, 44.97; C, 11.70; H, 1.36; N, 7.04.

**Preparation of Molybdenum(IV) and Tungsten(IV) and -(V) Hexaisothiocyanato Complexes.**—These complexes were prepared by stirring the starting materials in an appropriate solvent for a period of time. For the potassium salts of molybdenum(IV) and tungsten(IV), stoichiometric amounts of the appropriate halide and potassium thiocyanate were stirred in acetonitrile for 12–18 hr. The tungsten(V) complex was prepared from tungsten(V) chloride and potassium thiocyanate in ether. The tetrabutylammonium and tetraphenylarsonium compounds were prepared by treating the potassium salt of the thiocyanate complex with tetrabutyl- or tetraphenylarsonium chloride, respectively, in acetonitrile for *ca.* 2 hr. The insoluble KCl which formed as one of the products was removed by filtration and the solvent was removed from the desired product by vacuum distillation. The resulting complexes were dried under dynamic vacuum for *ca.* 24–72 hr. The analytical data are given in Table I.

The potassium salts were soluble in acetonitrile, slightly soluble in 1,2-dichlorethane and dichloromethane, and insoluble in benzene. The tetrabutyl- and tetraphenylarsonium salts were much more soluble than the potassium salts in the above solvents.

**Analytical Procedures.**—Carbon, hydrogen, nitrogen, arsenic, and sulfur analyses were performed by the Alfred Bernhardt Mikroanalytisches Laboratorium in Max-Plank-Institut für Kohlenforschung. Molybdenum and tungsten were analyzed in the normal manner by conversion to the oxide, $MO_3$.

**Physical Measurements.**—Infrared spectra (4000–200 $cm^{-1}$) and room-temperature magnetic susceptibility measurements were carried out using methods previously described.[13,14]

## Results and Discussion

The preparation of the hexaisothiocyanato complexes of molybdenum(IV) and tungsten(IV) was very similar to the preparation of the hexaisothiocyanato complexes of niobium(V) and -(IV) and tantalum(V) reported previously.[14] The preparation of the hexaisothiocyanato complexes of tungsten(V) offered special problems since they were readily reduced by the common high dielectric constant solvents such as alkyl cyanides and pyridine, which readily solvate potassium thiocyanate. A noncoordinating solvent, incapable of re-

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duction of the halides, and of high volatility was desirable. Ethyl ether was found to display these characteristics. Long reaction periods were required, however, since the solubility of potassium thiocyanate in ethyl ether was very limited. Although acetonitrile readily reduced tungsten(V) chloride to $WCl_4 \cdot 2CH_3CN$, it was found that when the metal was surrounded with six thiocyanate groups, reduction was inhibited. This was confirmed by the identical X-ray powder patterns and infrared spectra of pure $KW(NCS)_6$ and $KW(NCS)_6$ recovered after stirring with acetonitrile. Since the hexaisothiocyanatotungstate(V) anion is stable to reduction in acetonitrile, it was found to be a convenient solvent for the metathesis reaction of $KW(NCS)_6$ and $Bu_4NCl$ to form $Bu_4NW(NCS)_6$. Molybdenum(V) chloride appeared to undergo reduction to a lower oxidation state in the presence of potassium thiocyanate.

**Infrared Spectra.**—The positions, intensities, and band assignments of the complexes are summarized in Table II. Intense absorptions in the region of 1900–2200 $cm^{-1}$ are due to the $C{\equiv}N$ stretch. Several correlations are immediately obvious. It seems that since there are several absorptions present representing a variety of different $C{\equiv}N$ bond strengths in the potassium salts, packing of the solid is important. In solution these solid-state interactions disappear completely. The molar extinction coefficients $\epsilon$ of the $C{\equiv}N$ stretch absorptions for $K_2Mo(NCS)_6$, $K_2W(NCS)_6$, and $KW(NCS)_6$ are 1008, 1040, and 879 $M^{-1}$ $cm^{-1}$ per $NCS^-$ unit, respectively. The product of $\nu_{1/2}\epsilon$ gives values of $1.51 \times 10^4$, $4.14 \times 10^4$, and $6.85 \times 10^4$ $M^{-1}$ $cm^{-2}$, respectively. These are all higher than any reported for metal–sulfur bonded complexes[15] and support the assignment of metal–nitrogen bonding. There were no absorption bands found which could be ascribed to the carbon–sulfur stretch. The N–C–S bend which appears as a doublet at 484 and 470 $cm^{-1}$ in the free thiocyanate ion is raised slightly to 497, 494, and 489 $cm^{-1}$ in $W(NCS)_6^-$, $W(NCS)_6^{2-}$, and $Mo(NCS)_6^{2-}$, respectively. The vibrations at 305, 281, and 315 $cm^{-1}$ for $KW(NCS)_6$, $K_2W(NCS)_6$, and $K_2Mo(NCS)_6$, respectively, are assigned to the metal–nitrogen stretching frequencies. It has been suggested[16] that the isothiocyanates appear to have strong bands at values slightly above the metal–chlorine stretches in chloro complexes of the same symmetry whereas thiocyanate complexes give bands which fall approximately halfway between the corresponding chloro and bromo complexes. For the compounds described here the metal–nitrogen stretching frequencies are somewhat lower than predicted when comparing them with the analogous hexachlorides. For $K_2MoCl_6$ and $K_2WCl_6$, $\nu_3$(M–Cl) is located at 340 and 324 $cm^{-1}$, respectively.[17] Analogous results were obtained for the hexaisothiocyanates of zirconium(IV) and hafnium(IV).[18]

**Magnetic Susceptibility.**—Octahedral $d^1$ tungsten(V) complexes, having fairly large spin–orbit coupling constants, are expected to have their observed magnetic moments appreciably lower than the theoretical spin-only value of 1.73 BM. This is seen to be the case with $KW(NCS)_6$ which has a magnetic moment of 1.36 BM at room temperature. Tungsten(IV) complexes (*i.e.*, $d^2$ cases) have spin–orbit coupling constants of approximately 1050 $cm^{-1}$ and this again decreases the observed magnetic moment from the spin-only value of 2.83 BM. The magnetic moment of 1.54 BM obtained for $K_2W(NCS)_6$ is within the range observed for tungsten(IV) complexes.[19] The spin–orbit coupling constant for molybdenum(IV) is much lower than the value for the tungsten complexes and this would be expected to cause an increase in the observed magnetic moments. Observed magnetic moments for molybdenum(IV) complexes are of the order 2.2–2.6 BM.[19] The magnetic moments obtained for the molybdenum(IV) complexes (2.80 BM for $[Bu_4N]_2[Mo(NCS)_6]$ and 3.02 BM for $K_2Mo(NCS)_6$) are somewhat higher than the values usually obtained. In fact our preparation of $[C_5H_5NH]_2[Mo(NCS)_6]$ has a magnetic moment of 3.0 BM which is also high compared to the value of 2.45 BM reported by Williams and Mitchell.[10] These high values might be accounted for by the presence of small amounts of molybdenum(III) impurities, although we have no evidence for the presence of molybdenum(III) in any of our samples.

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