as methyl substitutions on the ammonium nitrogen are made. Attempts at isolating pure solutions of the glycinatochromium(III) product by ion exchange were frustrated by difficulties in achieving complete separation from hexaaquochromium(III).

Barrett[7] has found spectral evidence for the protonation of the acetatopentaamminecobalt(III) ion and attributes the decrease in its rate of chromous reduction as acidity increases to this effect. The absence of such an effect in the reduction of the glycinatopentaamminecobalt(III) ion is not surprising in light of a study of the aquation of this and other amino acid–pentaamminecobalt(III) complexes.[8] The rate constant for the aquation path first order in hydrogen ion concentration is considerably larger for L = acetate[9] than it is for L = glycine, *N*-methylglycine, or *N*,*N*,*N*-trimethylglycine; the electrostatic influence of the ammonium group is thought to hinder protonation of the coordinated carboxyl function.

Comparison of activation parameters for the Cr(II) reduction of the glycinato and acetato complexes shows that the slower reduction rate for the former complex may be attributed principally to an activation entropy value more negative by 5 eu. The qualitative difference in $\Delta S^{\ddagger}$ for the two reactions is consistent with expectations, as the activated complex for the chromous reduction of the glycinatopentaamminecobalt(III) ion must bear an extra positive charge. The factor of 4 decrease in room-temperature reduction rates from the glycinato to the *N*,*N*,*N*-trimethylglycinato complex is reflected in a difference of only 3 eu in $\Delta S^{\ddagger}$. Experiments with molecular models[7] have suggested that as long as at least one α hydrogen is present, a configuration can be found for which steric repulsions in the approach of chromous ion to acetatopentaamminecobalt(III) derivatives are not expected to differ significantly from one complex to the next.

Acknowledgment.—Financial support for this research by the Atomic Energy Commission, Grant No. AT-04-3-326, is gratefully acknowledged.

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Photochemical Substitution Reactions of Substituted Group VI Metal Carbonyls

BY G. SCHWENZER, M. Y. DARENSBOURG,* AND D. J. DARENSBOURG

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During the early 1960's Strohmeier[1] published several papers on the photochemical substitution reactions of metal carbonyls and their derivatives. More recently there has been additional interest in the photolysis of group VI metal carbonyls.[2–7] Most of these studies have centered around the photolysis of the parent hexacarbonyls and the nature of the species $M(CO)_5$ generated in these reactions. We have reported the photochemical reaction of $Mo(CO)_5NHC_5H_{10}$ with ^{13}CO to produce $Mo(CO)_4(^{13}CO)NHC_5H_{10}$, preferentially labeled in the equatorial positions.[8]

In this paper we report an extension of our initial study into the photolysis of substituted metal carbonyls to include photochemical substitution reactions of $M(CO)_5L$ compounds with Lewis bases as well as ^{13}CO (eq 1), where M = Cr, Mo, or W; L = an amine or

$$M(CO)_5L + L' \xrightarrow{h\nu} M(CO)_4LL' + CO \qquad (1)$$

phosphine; and L′ = an amine, phosphine, or ^{13}CO. The preparation of new mixed (phosphine–amine)metal tetracarbonyl compounds by this procedure is described within.

Studies have been made of the dependence of the stereochemistries of the products and rates of the substitution process on the nature of the ligands L and L′ and the wavelength region of the irradiation source. Correlation of the photochemical substitution process with the electronic spectra of the $M(CO)_5L$ compounds has also been initiated.

Experimental Section

Preparation and Purification of Materials.—The starting materials, $M(CO)_5L$ compounds, were prepared by photolysis of the corresponding $M(CO)_6$ in the presence of the appropriate entering ligand L. Purification was affected by recrystallization from hexane or chloroform–methanol solvents. Infrared spectra in the carbonyl region and melting points were in agreement with published data. Tetrahydrofuran was refluxed and distilled over $LiAlH_4$ under dry nitrogen.

All photochemical reactions were carried out in a cylindrical quartz vessel fitted with an internal water condenser to maintain the solutions at about 25°. The reaction mixtures were stirred by means of a magnetic stirrer and were kept under a dry nitrogen atmosphere during the irradiation period. A 550-W Hanovia mercury lamp was positioned at a constant distance (approximately 10 in.) from the reaction vessel and was enclosed with a Pyrex filter sleeve when desired. This filter sleeve has the absorption characteristics indicated in Figure 1. The general method employed for preparative-scale reactions is outlined below specifically for *cis*-$W(CO)_4[P(C_6H_5)_3]NC_5H_5$.

Preparation of *cis*-$W(CO)_4[P(C_6H_5)_3]NC_5H_5$.—In a quartz reaction vessel 0.6 g (1.0 mmol) of $W(CO)_5P(C_6H_5)_3$ and 2.0 g (25 mmol) of pyridine in 20 ml of freshly distilled THF were irradiated under a nitrogen atmosphere for approximately 0.5 hr. An infrared spectrum of the resultant bright yellow solution revealed the presence of 70–80% *cis*-$W(CO)_4[P(C_6H_5)_3]NC_5H_5$ in addition to the starting material $W(CO)_5P(C_6H_5)_3$.

The solvent was removed at room temperature under vacuum to yield a bright yellow solid. This material was extracted with hexane to remove excess $W(CO)_5P(C_6H_5)_3$, *cis*-$W(CO)_4LL'$ compounds being generally much less soluble in hexane than $W(CO)_5L$ compounds. The remaining yellow residue was dissolved in chloroform, the solution was filtered, and an equal

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[1] For an excellent review of this work see W. Strohmeier, *Angew. Chem., Int. Ed. Engl.*, **3**, 730 (1964).

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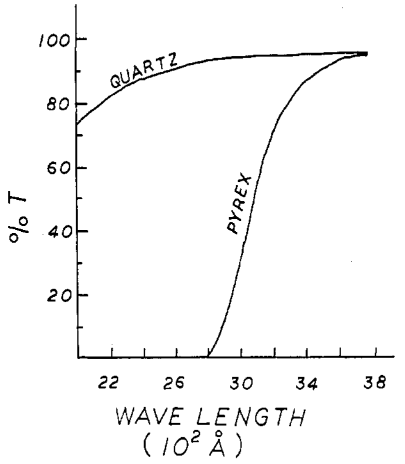

Figure 1.—Transmission characteristics of filter sleeves.

volume of methanol was added to the filtrate. Upon cooling this solution, bright yellow crystals were obtained and these were dried under vacuum. An infrared spectrum of these crystals in hexane in the carbonyl region contained four terminal CO stretching bands characteristic of *cis*-$M(CO)_4LL'$ species. *Anal.* Calcd for $W(CO)_4[P(C_6H_5)_3]NC_5H_5$: C, 50.89; H, 3.16. Found: C, 51.08; H, 3.17.

Quantitative-Yield Studies.—In a typical reaction designed to determine the yield of product, 60.4 mg (0.103 mmol) of $W(CO)_5P(C_6H_5)_3$ and 0.5 g (6.3 mmol) of pyridine were irradiated in 20 ml of THF as previously described. The tetrahydrofuran was removed under vacuum at room temperature and 50.0 ml of chloroform was added to dissolve completely the yellow solid residue. An infrared spectrum was then recorded of this solution and the yield of product was determined by comparison with a Beer's law plot of the pure product in chloroform.

^{13}CO-Enrichment Studies.—$M(CO)_5L$ (M = Mo, W; L = $P(C_6H_5)_3$, NHC_5H_{10}) compounds in THF contained in a Pyrex vessel over an atmosphere of 55% ^{13}CO (Isomet, Palisades Park, N. J.) were irradiated for approximately 20 min. The infrared spectra of the resulting products were determined in hexane solution.

Infrared Measurements.—Infrared spectral measurements were made on a Perkin-Elmer 521 spectrophotometer. The spectrophotometer was calibrated in the region above 2000 cm^{-1} against the spectrum of carbon monoxide and below 2000 cm^{-1} against the spectrum of water vapor.

Calculations.—Machine calculations were performed on a CDC 6400 at the State University of New York at Buffalo Computing Center. The frequencies necessary in assigning the ^{13}CO absorptions were calculated with an iterative computer program based on the work of Schachtschneider and Snyder[9] using an energy-factored block matrix for the carbonyl stretching vibrations. Agreement between calculated and observed frequencies was generally within ±1.0 cm^{-1}.

Results and Discussion

The photochemical preparations of $M(CO)_4L_2$ (M = Cr, Mo, W; L = triphenylphosphine; and M = W; L = tricyclohexylphosphine) and $M(CO)_4LL'$ (M = Mo, W; L = triphenylphosphine; L′ = pyridine, piperidine) are effected in good yields (approximately 75%) when decomposition of the product is minimized. For the $M(CO)_4LL'$ complexes, maximum yields are produced with irradiation times of only 30 min where no filter is used (see Figure 2). Both photochemical and thermal decomposition of the products serve to reduce the yield with longer reaction periods.

Infrared analyses of the disubstituted metal carbonyls indicate a trans structure for $Cr(CO)_4[P(C_6H_5)_3]_2$ and a cis configuration for the Mo and W complexes, with the exception of $W(CO)_4[P(C_6H_{11})_3]_2$ which has a trans configuration.[10] Four infrared-active ν(CO) vibrations are expected for a cis isomer, whereas only one infrared-active ν(CO) is expected for the trans isomer. The infrared stretching frequencies of the carbonyl groups of the new mixed-ligand complexes are reported in Table I and are compared to metal carbonyls containing N and P donor chelating ligands, of known cis configuration. Table II contains a summary of the photochemical substitution reactions investigated in this study, along with the stereochemistry of the resulting products.

It was impossible to isolate $Cr(CO)_4P(C_6H_5)_3$(amine) complexes under the same conditions as for the Mo and

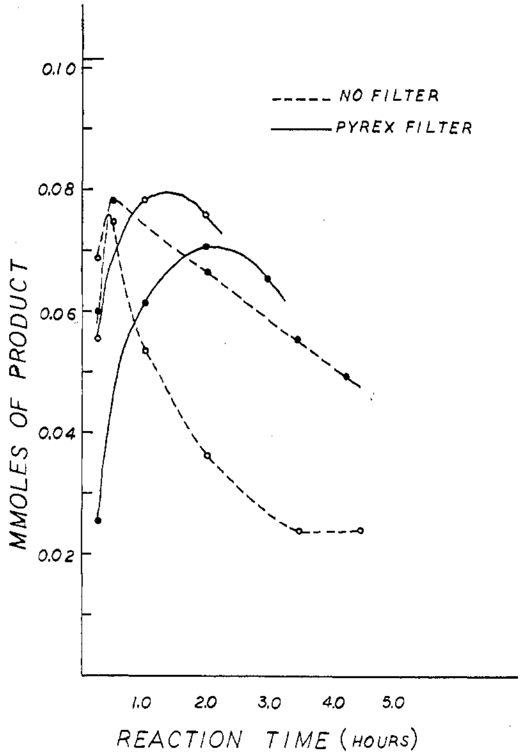

Figure 2.—Preparation of $W(CO)_4[P(C_6H_5)_3]$(amine) (amine = piperidine (○) and pyridine (●)) as a function of time and wavelength region irradiated (0.103 mmol corresponds to 100% yields)

TABLE I

INFRARED STRETCHING FREQUENCIES OF CARBONYL GROUPS IN MIXED-LIGAND COMPOUNDS[a]

Compd	CO vibrations, cm^{-1}			
	$A_1^{(2)}$	$A_1^{(1)}$	B_1	B_2
$Mo(CO)_5[P(C_6H_5)_3]NHC_5H_{10}$	2018 (m)	1906 (s)	1892 (s)	1852 (s)
$W(CO)_4[P(C_6H_5)_3]NHC_5H_{10}$	2011 (m)	1901 (s)	1881 (s)	1847 (s)
$Mo(CO)_4[P(C_6H_5)_3]NC_5H_5$	2017 (m)	1904 (s)	1889 (s)	1843 (s)
$W(CO)_4[P(C_6H_5)_3]NC_5H_5$	2011 (m)	1898 (s)	1878 (s)	1837 (s)
$Mo(CO)_4NP$[b,c]	2019 (m)	1905 (s)	1893 (s)	1849 (s)
$W(CO)_4NP$[c]	2013 (m)	1898 (s)	1884 (s)	1844 (s)
$W(CO)_4$diphos[d]	2018 (m)	1918 (s)	1899 (s)	1874 (s)
$W(CO)_4$TMEN[d]	2008 (m)	1880 (s)	1861 (s)	1820 (s)

[a] All frequencies listed were obtained in chloroform solutions. [b] NP = $(C_6H_5)_2PC_2H_4N(C_2H_5)_2$. [c] G. R. Dobson, R. C. Taylor, and T. D. Walsh, *Inorg. Chem.*, **6**, 1929 (1967). [d] diphos = $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$; TMEN = $(CH_3)_2NC_2H_4N(CH_3)_2$. C. L. Hyde, unpublished results. Absorptions for the diphos complex in dichloroethane have been reported by J. Chatt and H. R. Watson, *J. Chem. Soc.*, 4980 (1961), and for the TMEN complex in heptane by R. Poilblanc, *C. R. Acad. Sci.*, **256**, 4910 (1963).

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[10] It is possible that there is a small percentage (10%) of the trans isomer present in the $P(C_6H_5)_3$ derivatives of Mo and W; however, the cis isomer is the predominant product.

TABLE II

SUMMARY OF THE PHOTOCHEMICAL SUBSTITUTION REACTIONS OF $M(CO)_5L$ COMPOUNDS

Compd photolyzed	Entering ligand, L or L′	Stereochemistry of products
$Cr(CO)_5P(C_6H_5)_3$	$P(C_6H_5)_3$	*trans*-$Cr(CO)_4[P(C_6H_5)_3]_2$
$Cr(CO)_5P(C_6H_5)_3$	C_5H_5N or $C_5H_{10}NH$	(Unstable products)
$Mo(CO)_5P(C_6H_5)_3$	$P(C_6H_5)_3$	*cis*-$Mo(CO)_4[P(C_6H_5)_3]_2$[10]
$Mo(CO)_5NHC_5H_{10}$	$P(C_6H_5)_3$	*cis*-$Mo(CO)_4[P(C_6H_5)_3]NHC_5H_{10}$
$Mo(CO)_5P(C_6H_5)_3$	C_5H_5N	*cis*-$Mo(CO)_4[PC_6H_5)_3]NC_5H_5$
$Mo(CO)_5P(C_6H_5)_3$	$C_5H_{10}NH$	*cis*-$Mo(CO)_4[P(C_6H_5)_3]NHC_5H_{10}$
$Mo(CO)_5P(C_6H_5)_3$	^{13}CO	(Axially ^{13}CO enriched)
$W(CO)_5P(C_6H_5)_3$	$P(C_6H_5)_3$	*cis*-$W(CO)_4[P(C_6H_5)_3]_2$[10]
$W(CO)_5P(C_6H_{11})_3$	$P(C_6H_{11})_3$	*trans*-$W(CO)_4[P(C_6H_{11})_3]_2$
$W(CO)_5P(C_6H_5)_3$	C_5H_5N	*cis*-$W(CO)_4[P(C_6H_5)_3]NC_5H_5$
$W(CO)_5P(C_6H_5)_3$	$C_5H_{10}NH$	*cis*-$W(CO)_4[P(C_6H_5)_3]NHC_5H_{10}$
$W(CO)_5NHC_5H_{10}$	$P(C_6H_5)_3$	*cis*-$W(CO)_4[P(C_6H_5)_3]NHC_5H_{10}$
$W(CO)_5NC_5H_5$	$P(C_6H_5)_3$	*cis*-$W(CO)_4[P(C_6H_5)_3]NC_5H_5$
$W(CO)_5NHC_5H_{10}$	^{13}CO	(Equatorially ^{13}CO enriched)
$W(CO)_5P(C_6H_5)_3$	^{13}CO	(Axially ^{13}CO enriched)

W analogs; rather *trans*-$Cr(CO)_4[P(C_6H_5)_3]_2$ is the principal product formed. Evidently $Cr(CO)_4P(C_6H_5)_3$(amine) is quite unstable at room temperature, and loss of the amine leads to the formation of the highly reactive $[Cr(CO)_4P(C_6H_5)_3]$ moiety. Reaction with CO arising from adjacent molecules or reaction with free $P(C_6H_5)_3$ in solution thus forms the pentacarbonyl or the disubstituted, thermodynamically stable $Cr(CO)_4[P(C_6H_5)_3]_2$ product. Some infrared spectral evidence for the formation of the mixed-ligand complex was obtained for a reaction carried out at ∼−30°. It may, therefore, be possible to isolate mixed-ligand complexes of chromium at low temperatures.

These conjectures on the fate of the $Cr(CO)_4[P(C_6H_5)_3]$(amine) species are substantiated by decomposition studies performed on the isolable $Mo(CO)_4[P(C_6H_5)_3]NHC_5H_{10}$ analog. *cis*-$Mo(CO)_4[P(C_6H_5)_3]NHC_5H_{10}$ decomposes in solution at ambient temperatures of produce $Mo(CO)_5P(C_6H_5)_3$ and *cis*-$Mo(CO)_4[P(C_6H_5)_3]_2$, with the latter species being predominant (see eq 2 and 3).

$$\mathit{cis}\text{-}\underset{\text{I}}{Mo(CO)_4[P(C_6H_5)_3]NHC_5H_{10}} \longrightarrow \underset{\text{II}}{[Mo(CO)_4P(C_6H_5)_3]} + NHC_5H_{10} \qquad (2)$$

$$\text{II} + P(C_6H_5)_3 \text{ or } CO \longrightarrow \mathit{cis}\text{-}Mo(CO)_4[P(C_6H_5)_3]_2 + Mo(CO)_5P(C_6H_5)_3 \qquad (3)$$

($P(C_6H_5)_3$ and CO, as well as a metal-containing precipitate, are produced by decomposition of II.) The rate of decomposition is first order in $Mo(CO)_4[P(C_6H_5)_3]NHC_5H_{10}$ and much faster than that observed for the analogous reaction involving dissociation of piperidine from $Mo(CO)_5NHC_5H_{10}$.[11,12] For example, the first-order rate constant (k_1) is found to be 1.40×10^{-4} sec^{-1} at 45.4° in $Mo(CO)_5NHC_5H_{10}$[12] and 4.66×10^{-3} sec^{-1} at 42.3° in $Mo(CO)_4[P(C_6H_5)_3]NHC_5H_{10}$. However, the enthalpy of activation is quite similar for the two processes, with the $Mo(CO)_4[P(C_6H_5)_3]NHC_5H_{10}$ reaction having a slightly higher ΔH^* value.[13] Therefore, the difference in rates is primarily an entropy effect. This effect would be expected to be much larger for the smaller chromium-containing species.[14]

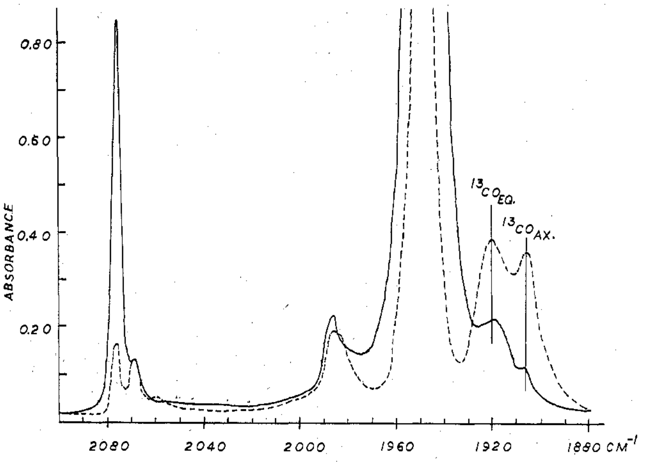

Figure 3.—Infrared spectra of $Mo(CO)_5P(C_6H_5)_3$ in hexane solution: —, ^{13}CO in natural abundance; - - -, ^{13}CO enriched. (A symmetrical band shape was assumed for the strong E mode vibration of $Mo(CO)_5P(C_6H_5)_3$ in determining the background absorptions beneath the ^{13}CO bands.)

cis-$W(CO)_4[P(C_6H_5)_3]$(amine) complexes were prepared in comparable yields by irradiating either $W(CO)_5P(C_6H_5)_3$ in the presence of piperidine or pyridine or $W(CO)_5$(amine) in the presence of $P(C_6H_5)_3$.[15] That the stereochemistry of $W(CO)_4[P(C_6H_5)_3]$(amine) complexes is the same regardless of the starting material is in constrast to the photochemical ^{13}CO substitution reactions of $W(CO)_5L$. $W(CO)_5$(piperidine) reacts photochemically with ^{13}CO preferentially labeling the equatorial carbonyls. (This is analogous to our result reported earlier for $Mo(CO)_5$(piperidine).[8]) It is, however, the axial carbonyl that is preferentially labeled in the photochemical reactions of W- or $Mo(CO)_5P(C_6H_5)_3$ with ^{13}CO.

The enrichment of the axial position in $M(CO)_5P(C_6H_5)_3$ (M = Mo, W) is approximately twice that of the equatorial positions after consideration is taken of statistical factors. This is evident from a comparison of the ratios of the lowest energy (A′) band in the equatorially monosubstituted ^{13}CO with that of the A_1 in the axially monosubstituted ^{13}CO. The relative percentage enrichment is normalized to the ratio observed in the natural-abundance ^{13}CO species (Figure 3). The comparable enrichment of the equatorial positions in $M(CO)_5NHC_5H_{10}$ (M = Mo, W) is approximately 3 times as great as the enrichment of the axial position after consideration of statistical factors.[8]

These isotopic substitution studies, therefore, indicate that the principal product, *cis*-$M(CO)_4[P(C_6H_5)_3]$(amine), obtained from irradiation of $M(CO)_5P(C_6H_5)_3$ in the presence of amines probably results from an isomerization process. Similar isomerization processes would explain the resultant *cis*-$M(CO)_4[P(C_6H_5)_3]_2$ (M = Mo, W) product obtained from the photochemical reactions of $M(CO)_5P(C_6H_5)_3$ in the presence of triphenylphosphine. This is evident in that isomerically

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[11] D. J. Darensbourg and T. L. Brown, *Inorg. Chem.*, **7**, 1679 (1968).

[12] R. J. Dennenberg and D. J. Darensbourg, *ibid.*, **11**, 72 (1972).

[13] The details of these and related kinetic studies will be the subject of a later publication.

[14] The rate of dissociation of piperidine from $Cr(CO)_5NHC_5H_{10}$ is similar to that of the molybdenum analog, $k_1 = 1.03 \times 10^{-4}$ sec^{-1} at 45.4°.[11]

[15] Accurate band shape analyses of the overlapping low-energy CO vibrations clearly indicate the presence of only three bands, confirming the cis structure for these compounds: C. L. Hyde, of this laboratory, unpublished results.

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 ~ 0.05 and ~ 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.

Acknowledgments.—We are most grateful to the donors of the Petroleum Research Fund administered by the American Chemical Society for financial support of this project. We also thank the Faculty of Natural Science and Mathematics of the State University of New York at Buffalo for Institutional Funds (National Institutes of Health) which in part purchased the photochemical equipment. Generous gifts of molybdenum and tungsten hexacarbonyls from Climax Molybdenum Co. are also acknowledged.

[16] We are thankful to a reviewer for pointing this out.

[17] D. J. Darensbourg and T. L. Brown, *Inorg. Chem.*, **7**, 959 (1968).

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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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