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Solution Photosubstitution Chemistry of Amine Pentacarbonyl Derivatives of the Group 6B Metals in the Presence of ^{13}CO. An Example of Stereospecific Incorporation of ^{13}CO

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The ligand photosubstitution chemistry of $M(CO)_5$(amine) derivatives (M = Cr, Mo, W; amine = piperidine, pyridine) in the presence of ^{13}C-labeled carbon monoxide has been demonstrated to involve both CO and amine loss at 366 and 313 nm. The relative quantum yields for CO vs. unique ligand (amine) dissociation were found to be highly dependent on the metal center, with the chromium complexes exhibiting a greater propensity for CO dissociation as opposed to amine loss. On the other hand, molybdenum and tungsten were shown (consistent with and as an extension of previous studies) to undergo amine dissociation with a greater quantum efficiency than CO loss. More importantly, it has been clearly established that for the process involving CO photosubstitution with ^{13}CO the products are stereospecifically labeled metal pentacarbonyl derivatives, *cis*-$M(CO)_4(^{13}CO)$(amine). These experiments demonstrate that there is either exclusively equatorial carbonyl photosubstitution occurring (affording a C_s intermediate) or a facile rearrangement of the C_{4v} form of the intermediate, $[M(CO)_4$(amine)], to the C_s structure prior to recombination with an incoming ^{13}CO ligand.

Introduction

The ligand photosubstitution chemistry of $M(CO)_5L$ complexes, where M = Mo or W and L = amine, has been demonstrated to involve both CO and L substitution via a dissociative mechanism with M–L cleavage (eq 1) and not M–CO cleavage (eq 2) being dominant.[1-3] Wavelength-dependent quantum yield studies indicate that CO substitution becomes more important at shorter excitation wavelengths.[2,4,5]

$$M(CO)_5L + CO \xrightarrow{h\nu} M(CO)_6 + L \qquad (1)$$

$$M(CO)_5L + L' \xrightarrow{h\nu} M(CO)_4LL' + CO \qquad (2)$$

We have previously reported stereoselective incorporation of ^{13}CO into $M(CO)_5L$ derivatives (M = Mo, W; L = NHC_5H_{10}) upon broad-wavelength irradiation of the substrates in the presence of labeled carbon monoxide in tetrahydrofuran.[6,7] In this paper we present results on the quantum efficiency for reactions 1 and 2 carried out in the presence of ^{13}CO where both M–L and M–CO cleavage could be observed simultaneously, i.e., as noted by the appearance of $M(CO)_5(^{13}CO)$ and $M(CO)_4(^{13}CO)L$. These studies were performed at excitation wavelengths of 313 and 366 nm where CO loss is expected to be enhanced. In contrast to the earlier reports for molybdenum and tungsten derivatives,[1-3] we found in the chromium analogues that M–CO bond rupture proceeds with a quantum efficiency equal to or greater than that of M–N bond dissociation at 313 and 366 nm for amine = NHC_5H_{10} or NC_5H_5. Furthermore, it is shown that reactions involving CO photosubstitution yield the stereospecifically labeled metal pentacarbonyl derivatives *cis*-$M(CO)_4(^{13}CO)$(amine).

Experimental Section

Materials. Reagent grade hexane was distilled under nitrogen from calcium sulfate (no special precautions were used to remove trace olefins). Molybdenum and tungsten hexacarbonyls were generous gifts from Climax Molybdenum Corp., whereas chromium hexacarbonyl was purchased from Strem Chemicals. Piperidine and pyridine were reagent grade chemicals obtained from Aldrich and Baker Chemical Co., respectively. ^{13}CO gas enriched to >90% was acquired from Prochem, B.O.C. Ltd., London.

Compound Preparations. The metal pentacarbonyl amine complexes were prepared photochemically in an Ace Glass circular photochemical reaction vessel from the metal hexacarbonyls with excess amine in THF.[8] After removal of solvent, excess $M(CO)_6$ was recovered by vacuum sublimation at 35–50 °C. The bright yellow products were purified by recrystallization from hexane at −79 °C.

Instrumentation. The infrared spectra were recorded on a Perkin-Elmer 521 spectrophotometer equipped with a linear absorbance potentiometer. The spectra were calibrated against a water-vapor spectrum below 2000 cm^{-1} and against a CO spectrum above 2000 cm^{-1}. Sodium chloride solution cells (1.0-mm path length) were used with hexane solvent in the reference cell. Ultraviolet–visible spectra were recorded on a Cary 14 recording spectrophotometer using 1-cm quartz cells.

Sample Preparation. All samples were handled under red, photographic safe light during mixing and throughout analysis. Typically, a 25-mL solution of reactants was prepared and mixed thoroughly.

Three-milliliter aliquots of solution were pipetted into 13 × 100 mm Pyrex test tubes, which were sealed with tight-fitting rubber serum caps secured by copper wire. The tubes were then degassed by three freeze–thaw cycles. Pumping was accomplished by inserting syringe needles connected to a common vacuum line through the serum caps. Tubes for a particular experiment were simultaneously degassed in a batch of four to six. Upon completion of degassing, 90% ^{13}CO was admitted to a positive pressure. The samples were kept at −79 °C and in the dark at all times except when being irradiated or analyzed to avoid thermal decomposition.

Samples were temperature equilibrated (25 °C) prior to irradiation. An unirradiated blank was always employed in establishing a baseline for the analytical procedures. Reactant concentrations (5×10^{-3} M) were arranged so as to yield optical densities much greater than 2 in a 1.0-cm cell at the appropriate wavelength.

Quantum Yield Determination. Quantum yields were determined using a photochemical reactor with a merry-go-round feature. The turntable photochemical reactor was purchased from Ace Glass Inc. and was fitted with a Pyrex water jacket through which circulated coolant (water or filter solutions) between the lamp and the sample tubes.

The light source was a 450-W Hanovia medium-pressure mercury-vapor lamp. For the irradiations at 366 nm, the extraneous lines of the lamp were filtered out using (a) a uranium glass filter sleeve from Ace Glass Inc. and (b) Corning plate glass filters no. 5840. Ultraviolet–visible spectra indicated good isolation of the 366-nm line. Light intensity at this wavelength was approximately 2×10^{15} quanta s^{-1} cm^{-2}.

Isolation of the 313-nm line was achieved employing a set of Corning filters no. 9863 in addition to a three-component solution consisting of 0.89 M $NiSO_4$, 2.5×10^{-3} M K_2CrO_4, and 0.123 M potassium biphthalate in water.[9] This filter solution was circulated through the water jacket by means of a small-tubing pump. The circulation system was closed with a filter flask serving as a heat exchanger as well as a reservoir. The transmission characteristics of the filter solution were carefully monitored spectroscopically. Light intensity at this wavelength was 8×10^{14} quanta s^{-1} cm^{-2}.

Product quantum yields were determined by quantitative infrared spectroscopy, employing peak heights, in the $\nu(CO)$ region. Quantum yields were computed from the appearance of well-isolated $\nu(CO)$ absorptions. The extinction coefficients for the intense T_{1u} vibrations in the $M(^{12}CO)_6$ derivatives were determined from a Beer's law plot which had been subjected to a linear least-squares fit. The extinction coefficients for the E vibration in the $M(^{12}CO)_5(^{13}CO)$ species (which is degenerate with the T_{1u} mode in $M(^{12}CO)_6$) were in turn calculated by multiplying the values obtained for the T_{1u} vibrational modes by 0.667.[10] On the other hand, the extinction coefficients for the vibrations centered at ~1900 cm^{-1} in the metal pentacarbonyl amine derivatives, attributed to a mono-^{13}CO equatorially substituted species, were obtained from the 4% of these molecules which are present in natural-abundance samples. All quantum efficiencies were measured before 10% reaction had occurred.

Actinometry. Light intensity was gauged by potassium ferrioxalate actinometry using the procedure described by Calvert and Pitts.[11] A Beer's law plot for the absorption of the $Fe(1,10\text{-}phen)_3^{2+}$ complex was constructed which yielded an extinction coefficient of 1.06×10^4 L/(mol cm) as compared to the reported value of 1.11×10^4 L/(mol cm).[11] In practice the actinometer system showed good linearity with irradiation time and good reproducibility.

Vibrational Analysis in the ν(CO) Region. Initial CO stretching force constant calculations on $M(CO)_6$ and $M(CO)_5$(amine) derivatives were performed using the Cotton–Kraihanzel approach[12] employing frequency data obtained in a hydrocarbon solvent. The trial force constants were refined using the ^{13}CO frequency data and an iterative computer program[13] that adjusts a set of force constants common to a group of isotopically substituted molecules to give simultaneously a least-squares fit between the observed and calculated frequencies for all of the molecules. Force constants were refined in general to reproduce the observed ^{12}CO and ^{13}CO vibrations to within an average error of <1.5 cm^{-1}.

Results and Discussion

Electronic Structure. Figure 1 contains the low-energy absorption bands in the room-temperature electronic spectra of the metal pentacarbonyl amine derivatives investigated. The electronic spectra of these derivatives, especially those of molybdenum and tungsten, have been previously discussed in the literature.[1-3,14,15] The ground electronic state of $M(CO)_5L$ species, $^1A_1$, has been assigned a $b_2^2e^4$ configuration.[16] The low-energy, weak absorptions observed at ~440 nm in the tungsten derivatives, which are, however, not seen in the chromium and molybdenum analogues, have been attributed to the spin-forbidden ligand field transition $^1A_1(b_2^2e^4) \rightarrow {}^3E(b_2^2e^3a_1^1)$. However, the stronger absorptions ($\epsilon \sim$ 4000–7000) centered at ~400 and 380 nm in the piperidine and pyridine derivatives, respectively, have been assigned to the corresponding spin-allowed $^1A_1 \rightarrow {}^1E$ transition. As is readily seen in Figure 1, this absorption occurs at slightly lower energy in the chromium derivatives than in the molybdenum and tungsten analogues. On the other hand, the absorptions at the somewhat higher energies of ~340 nm are believed to be due primarily to the spin-allowed, orbitally allowed, $^1A_1(b_2^2e^4) \rightarrow {}^1E(b_2^2e^3b_1^1)$ and/or spin-allowed, orbitally forbidden, $^1A_1(b_2^2e^4) \rightarrow {}^1A_2(e^4b_2^1b_1^1)$ transitions.[2] Higher energy absorptions (>300 nm) can be ascribed to $M \rightarrow \pi^*$ CO charge-transfer transitions.

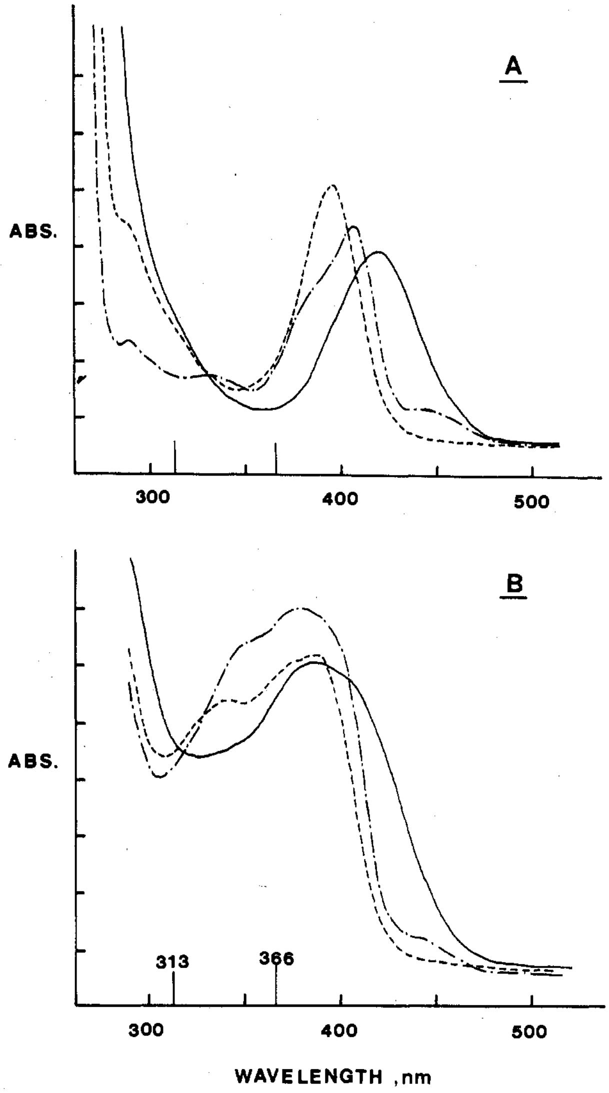


Figure 1. Low-energy absorptions in room-temperature electronic spectra in hexane (concentration 10^{-4} M in 1.0-cm cell). (A) $M(CO)_5(NHC_5H_{10})$: —, M = Cr; - - -, M = Mo; –·–, M = W. (B) $M(CO)_5(NC_5H_5)$: —, M = Cr; - - -, M = Mo; –·–, M = W.

Wrighton, Hammond, and Gray,[1] and more recently Dahlgren and Zink,[3] have proposed that there are excited states which yield ligand labilization along either the *xy* axes or the *z* axis. For example, population of the $\sigma_z^*(b^2e^4 \rightarrow$

Table I. Calculated and Observed CO Stretching Frequencies in ^{13}CO-Enriched $Cr(CO)_6$[a]

Molecule	Freq, cm^{-1}					
All-^{12}CO	2109.2	2015.0	2015.0	1987.2 (1987.1)	1987.2	1987.2
Mono-^{13}CO	2103.5	2007.5 (2007.5)	2015.0	1987.2 (1987.1)	1987.2	1955.5 (1955.6)

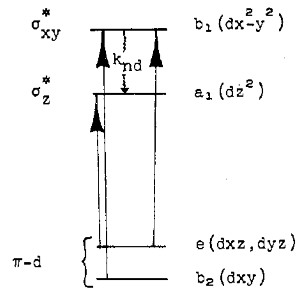
[a] Spectra were determined in hexane solvent. The refined CO force constants calculated were $k = 16.43_0$, $k_c = 0.26_2$, and $k_t = 0.48_6$, with an average error in frequencies of 0.1 cm^{-1} or 0.004%. See also R. N. Perutz and J. J. Turner, *Inorg. Chem.*, 14, 262 (1975), and references therein.

Table II. Calculated and Observed CO Stretching Frequencies in ^{13}CO-Enriched $Cr(CO)_5(NHC_5H_{10})$[a]

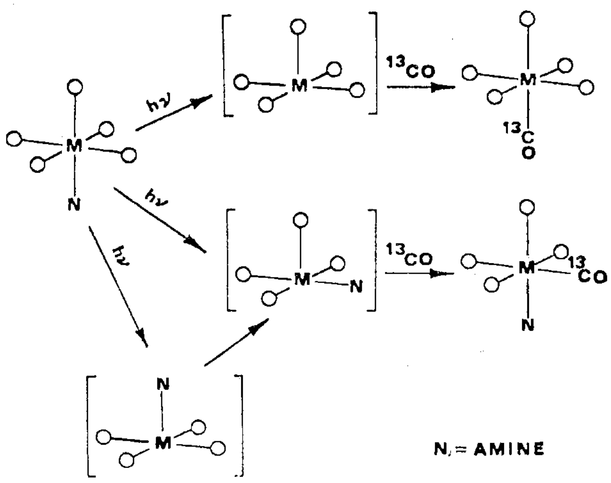
Molecule	Freq, cm^{-1}				
All-^{12}CO	2066.5 (2066.8)	1979.4	1933.4 (1933.5)	1933.4 (1933.5)	1916.3 (1916.2)
Mono-^{13}CO (eq)	2058.5 (2058.9)	1971.9	1933.4 (1933.5)	1903.5 (1902.7)	1917.8 (1917.8)
Mono-^{13}CO (ax)	2063.4	1979.4	1933.4 *b*	1933.4 *b*	1876.5 (1876.7)[c]
Di-^{13}CO (eq) (cis)	2048.9 (2050.0)[d]	1966.1 (1965.4)	1903.8	1903.2	1919.1
Di-^{13}CO (eq) (trans)	2050.6 (2050.0)[d]	1953.8	1933.4 *b*	1890.4 (1890.0)	1912.9

[a] Spectra were determined in heptane solvent. The refined CO force constants calculated were $k_1 = 15.03_1$, $k_2 = 15.76_1$, $k_{c'} = 0.30_5$, $k_c = 0.33_6$, and $k_t = 0.66_8$, with an average error in frequencies of 0.4 cm^{-1} or 0.021%. [b] These vibrations are degenerate with those in all-^{12}CO and mono-^{13}CO equatorial species. [c] Observed only at very high concentrations, i.e., due to ^{13}C at natural-abundance levels. [d] Only a single absorption was noted at 2050.0 cm^{-1} assignable to both of the di-^{13}CO equatorial species.

Scheme I



Scheme II



$b_2{}^2e^3a_1{}^1$) level strongly labilizes exclusively σ-donor ligands, e.g., amines, whereas population of the $\sigma_{xy}{}^*(e^4b_2{}^2 \rightarrow e^4b_2{}^1b_1{}^1$ or $e^4b_2{}^2 \rightarrow b_2{}^2e^3b_1{}^1$) level results in labilization of *equatorial* CO groups. These assignments are reproduced in Scheme I, where k_{nd} is the rate constant for internal conversion between the upper and lower excited states.

We have indeed provided the only experimental evidence in support of the proposal for equatorial CO loss in our experiments illustrating ^{13}CO incorporation into an equatorial position stereoselectively upon broad-wavelength irradiation of $M(CO)_5(NHC_5H_{10})$ (M = Mo, W) in the presence of ^{13}CO.[6,7] However, it is crucial to arguments such as those provided above to examine these processes quantitatively at specific wavelengths for a variety of metals and amine ligands in order to more clearly define the stereochemical position of an incoming ^{13}CO ligand as well as the relative quantum efficiency for M–CO and M–amine bond dissociation. With this in mind we have investigated these photochemical processes at 366 and 313 nm where absorptions into the tails of these two principal ligand field bands occur.

ν(CO) Infrared Analysis. Infrared spectroscopy was used to quantitatively follow the production of $M(CO)_5(^{13}CO)$ and $M(CO)_4(^{13}CO)$(amine) species prepared photochemically via dissociative loss of amine or ^{12}CO. In addition, an analysis of the ν(CO) spectra in the isotopically labeled pentacarbonyl amine derivatives is necessary in order to determine the stereochemical position of an incoming ^{13}CO ligand. Figure 2A depicts the ν(CO) spectrum of *cis*-$Cr(CO)_4(^{13}CO)(NHC_5H_{10})$ prepared thermally from *cis*-$Cr(CO)_4[NHC_6H_{10}]_2$ and ^{13}CO, whereas Figure 2B illustrates the changes in the ν(CO) spectral region of $Cr(CO)_5(HNC_5H_{10})$ upon photolysis in the presence of ^{13}C-enriched carbon monoxide. Tables I and II contain the calculated and observed ν(CO) values for representative $M(CO)_5(^{13}CO)$ and $M(CO)_4(^{13}CO)(NHC_5H_{10})$ species, where M = Cr. As is readily discernible from Figure 2 and Table II, the only ν(CO) bands which are enhanced in the photochemical incorporation of ^{13}CO into $Cr(CO)_5(NHC_5H_{10})$ can be ascribed to equatorially substituted ^{13}CO species. For example, bands labeled a (at 1965.4, 1902.7, and 1890 cm^{-1}) in Figure 2, which are attributed to ^{13}CO equatorially substituted species, become increasingly more intense with CO substitution while the band labeled b (at 1876.7 cm^{-1}) which is due to the mono-^{13}CO axial species remains unaffected. Careful quantitative infrared measurements indicated that the maximum level of ^{13}CO incorporation into the axial position which could have occurred is less than 5% of the total amount of mono-^{13}CO-substituted species afforded. In other words, the error limit in our ability to detect small quantities of *trans*-$Cr(CO)_4(^{13}CO)(NHC_5H_{10})$ is <5% of all molecules enriched with a single ^{13}CO group. Similar spectral changes were noted in the ν(CO) spectra for the other sample investigated in this study.

Ligand Photosubstitution Reactions. Irradiation of $M(CO)_5$(amine) complexes (M = Cr, Mo, W; amine = NHC_5H_{10}, NC_5H_5) at 366 and 313 nm in saturated hydro-

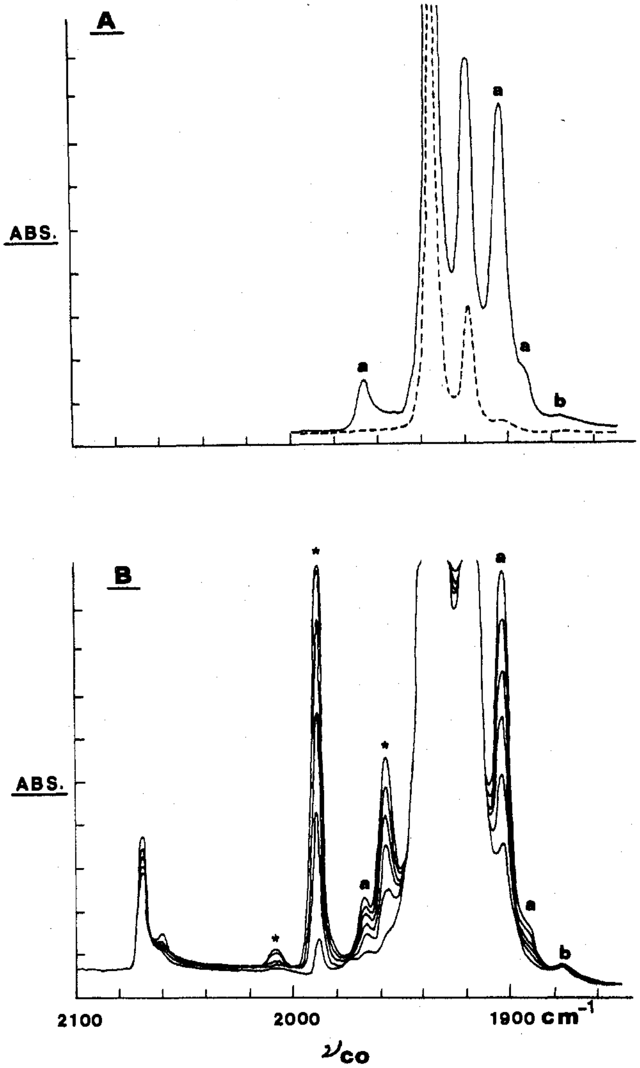


Figure 2. ν(CO) spectra in hexane solution. (A) Spectra for (- - -) $Cr(CO)_5(NHC_5H_{10})$ and (—) *cis*-$Cr(CO)_4(^{13}CO)(NHC_5H_{10})$. (B) Time-dependent traces of photochemical reaction of $Cr(CO)_5(NHC_5H_{10})$ with ^{13}CO. Bands labeled with an asterisk are those of $Cr(CO)_5(^{13}CO)$ while the others are due to *cis*-$Cr(CO)_4(^{13}CO)(NHC_5H_{10})$.

Table III. Photosubstitution Quantum Yields for Metal Pentacarbonyl Amine Derivatives with ^{13}CO as Entering Ligand[a]

Complex	Product	Quantum yield 366 nm	Quantum yield 313 nm
$Cr(CO)_5NHC_5H_{10}$	$Cr(CO)_5(^{13}CO)$	0.23	0.14
	cis-$Cr(CO)_4(^{13}CO)NHC_5H_{10}$	0.23	0.30
$Mo(CO)_5NHC_5H_{10}$	$Mo(CO)_5(^{13}CO)$	0.42	0.18
	cis-$Mo(CO)_4(^{13}CO)NHC_5H_{10}$	0.12	0.15
$W(CO)_5NHC_5H_{10}$	$W(CO)_5(^{13}CO)$	0.35	0.20
	cis-$W(CO)_4(^{13}CO)NHC_5H_{10}$	0.04	0.09
$Cr(CO)_5NC_5H_5$	$Cr(CO)_5(^{13}CO)$	0.19	0.17
	cis-$Cr(CO)_4(^{13}CO)NC_5H_5$	0.20	0.24
$Mo(CO)_5NC_5H_5$	$Mo(CO)_5(^{13}CO)$	0.25	
	cis-$Mo(CO)_4(^{13}CO)NC_5H_5$	0.11	0.10
$W(CO)_5NC_5H_5$	$W(CO)_5(^{13}CO)$	0.28	0.32
	cis-$W(CO)_4(^{13}CO)NC_5H_5$	0.01	0.04

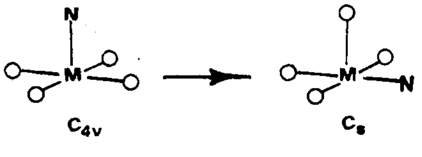
[a] All reactions were carried out in hexane. Quantum yields are for appearance of product with an error estimated at ±10%. Solutions were saturated with ^{13}CO at a pressure of about 1.5 atm.

carbon solvent in the presence of ^{13}CO resulted in both amine and CO photodissociation with the latter process affording stereospecifically labeled ^{13}CO derivatives *cis*-$M(CO)_4(^{13}CO)$(amine). These observations are summarized in Scheme II. Product quantum yields are listed in Table III.

For all three metals there was an enhancement of CO photodissociation with a concomitant decrease in amine photodissociation upon population of the higher ligand field state (i.e., irradiation at 313 vs. 366 nm), where labilization along the *xy* axes occurs. As has been previously noted for the molybdenum and tungsten derivatives, M–amine photodissociation occurs with a greater quantum efficiency than M–CO bond cleavage for both saturated and unsaturated amines upon irradiation at 366 or 313 nm.[1,2] Although the overall quantum yield decreased slightly on going from molybdenum to tungsten, the relative quantum efficiency for amine to CO photodissociation *increased* in going down the series.[17] *This metal dependence is of particular significance in that for the first member of the group 6B metals, chromium, the quantum yield for metal–CO photodissociation is equal to or greater than that for metal–amine photodissociation at both 366 and 313 nm.*[18] It is therefore necessary to carefully qualify any statements regarding the generalization that metal pentacarbonyl amine photochemistry is characterized by highly efficient M–amine, and not M–CO bond dissociation. We can offer no definitive explanation for this trend at this time.[19] The diminution in photoreactivity of the M–CO bond as one proceeds down the metal series Cr > Mo > W does not parallel M–amine (Cr ~ Mo > W) nor M–CO (Cr ~ W < Mo) thermal dissociation rates.

As indicated in Scheme II, based on data as described in Figure 2B, *the stereochemical position of an incoming ^{13}CO ligand in that portion of the photochemistry involving CO dissociation is exclusively* cis *to the amine ligand.* This product results from reaction of ^{13}CO with the stable form of the [$M(CO)_4$(amine)] intermediate which is assumed to be the C_s isomer where the amine ligand is in the equatorial plane of the square-pyramidal structure. Evidence for the C_s isomer being the ground-state structure for the [$M(CO)_4$(amine)] intermediate has been provided in that (a) *cis*-$M(CO)_4$(amine)$_2$ species thermally react with ^{13}CO to afford pure *cis*-$M(CO)_4(^{13}CO)$(amine) derivatives,[20] (b) *fac*-$M(CO)_3(C_5H_5N)_3$ complexes react with ^{13}CO to yield *fac*-$M(CO)_3(^{13}CO)_2(C_5H_5N)$ species,[20] and (c) *fac*-$M(CO)_3(^{13}CO)$(diamine) complexes react via a ring-opening process with L to give *fac*-$M(CO)_3(^{13}CO)L_2$ derivatives.[21,22] These experiments clearly illustrate that not only is the stable form of the [$M(CO)_4$(amine)] intermediate the C_s isomer but also this intermediate does not scramble CO groups during its lifetime in solution.

Scheme II takes into consideration the possibility that the photochemically afforded, stereospecifically labeled derivatives *cis*-$M(CO)_4(^{13}CO)$(amine) can arise in total or in part from a facile rearrangement of the C_{4v} isomeric form of the [$M(CO)_4$(amine)] intermediate to its C_s form prior to recombination with CO. Unfortunately, little is known concerning the rates of rearrangements of the type



On the other hand, Kelly et al. have reported that $Cr(CO)_5$, generated by flash photolysis of $Cr(CO)_6$, reacts with CO in cyclohexane solution with a bimolecular rate constant of $(3 \pm 1) \times 10^6$ M^{-1} s^{-1}.[23] Further studies have indicated that this rate constant increases as the nucleophilicity of the incoming ligand increases, with rate constants ranging from 7.0×10^6 M^{-1} s^{-1} (for benzene) to 1.6×10^8 M^{-1} s^{-1} (for acetonitrile).[24] The latter rate constant differs from the diffusion-controlled rate constant in cyclohexane of 6.6×10^9 M^{-1} s^{-1} by only 1 order of magnitude.[11] In other words, these 16-electron group 6B metal derivatives are indeed quite reactive; e.g., $Cr(CO)_5$ would have an average characteristic inverse lifetime in CO-saturated cyclohexane solution[25,26] of 3×10^6[CO] or $\sim 3 \times 10^4\ s^{-1}$.[27] This reactivity of group 6B pentacoordinate species has as well been demonstrated in the rather indiscriminate behavior of these derivatives toward various incoming bases in competitive studies carried out by conventional techniques.[28,29]

Therefore, in order for the photochemical reaction of $M(CO)_5$(amine) with ^{13}CO to yield exclusively the *cis*-$M(CO)_4(^{13}CO)$(amine) species via a process involving the C_{4v} isomer of $[M(CO)_4(amine)]$ to some extent, the rate constant for intramolecular rearrangement ($C_{4v} \rightarrow C_s$) must be greater than $3 \times 10^4\ s^{-1}$, assuming $[Cr(CO)_5]$ and $[Cr(CO)_4(amine)]$ to be of comparable reactivity.

There is evidence which indicates that the lifetime of the C_{4v} isomers of $[M(CO)_4PPh_3]$ (M = Cr, Mo) is of the same order of magnitude as the rate of rearrangement to the more favored C_s intermediate. Cohen and Brown[30] have observed by ^{13}C NMR that $[Cr(CO)_4PPh_3]$, produced by thermal dissociation of PPh_3 from *trans*-$Cr(CO)_4[PPh_3]_2$, reacts with ^{13}CO to afford a mixture of *cis*- and *trans*-$Cr(CO)_4(^{13}CO)PPh_3$. Similarly, we have recently shown that *trans*-$Mo(CO)_4[PPh_3]_2$ readily dissociates PPh_3 both thermally[31] and photochemically[32] to yield $[Mo(CO)_4PPh_3]$ which combines with ^{13}CO to give a mixture of *cis*- and *trans*-$Mo(CO)_4(^{13}CO)PPh_3$, with the latter isomer constituting ~20% of the isomeric mixture obtained. Nevertheless, the $[M(CO)_4PPh_3]$ fragment may be much different from the $[M(CO)_4(amine)]$ intermediate since the PPh_3 ligand is different from an amine ligand in its ability to stabilize the coordinatively unsaturated fragment in a C_{4v} geometry.[33]

It is therefore very likely that the lack of observing even trace quantities (<5% of the total isotopically enriched species) of *trans*-$M(CO)_4(^{13}CO)$(amine) species in the photosubstitution chemistry of $M(CO)_5$(amine) derivatives in the presence of ^{13}CO is the result of an exclusive loss of an equatorial CO ligand in the primary photochemical process. However, in order to *assert* that there is no loss of the axial CO ligand in Scheme II it will be necessary to prepare a relative pure axially labeled $M(CO)_5$(amine) species and subject it to photolysis in the presence of ^{12}CO. Thus far, we have not been able to devise a synthesis of this species.[34]

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Registry No. $Cr(CO)_6$, 13007-92-6; $Cr(CO)_5(^{13}CO)$, 17594-10-4; $Cr(CO)_5(NHC_5H_{10})$, 15710-39-1; *cis*-$Cr(CO)_4(^{13}CO)(NHC_5H_{10})$, 65255-66-5; *trans*-$Cr(CO)_4(^{13}CO)(NHC_5H_{10})$, 65620-49-7; *fac*-$Cr(CO)_3(^{13}CO)_2(NHC_5H_{10})$, 65620-48-6; *mer*-(*trans*)-$(CO)_3(^{13}CO)_2(NHC_5H_{10})$, 65545-49-5; $Mo(CO)_5(NHC_5H_{10})$, 19456-57-6; $W(CO)_5(NHC_5H_{10})$, 31082-68-5; $Cr(CO)_5(NC_5H_5)$, 14740-77-3; $Mo(CO)_5(NC_5H_5)$, 14324-76-6; $W(CO)_5(NC_5H_5)$, 14586-49-3; $Mo(CO)_5(^{13}CO)$, 17594-07-9; *cis*-$Mo(CO)_4(^{13}CO)(NHC_5H_{10})$, 65255-67-6; $W(CO)_5(^{13}CO)$, 17594-12-6; *cis*-$W(CO)_4(^{13}CO)(NHC_5H_{10})$, 65255-68-7; *cis*-$Cr(CO)_4(^{13}CO)(NC_5H_5)$, 65545-51-9; *cis*-$Mo(CO)_4(^{13}CO)(NC_5H_5)$, 65255-69-8; *cis*-$W(CO)_4(^{13}CO)NC_5H_5$, 65545-50-8.

References and Notes

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(17) Wrighton[2] has previously made a similar observation.
(18) The relative quantum efficiency for Cr–CO vs. Cr–N dissociation is, however, expected to be reversed as one proceeds to larger wavelengths; e.g., at 313 nm the ratio (M–CO):(M–N) is ~2, whereas at 366 nm the ratio has already decreased to a value of ~1.
(19) A reviewer has pointed out that examination of the reported absorption spectra (at least for the piperidine derivatives) shows that neither 313- nor 366-nm excitation is directed into the amine-labilizing $^{1,3}E$ states for Cr but that 366-nm excitation is for Mo and W. Thus, it is reasonable to assume that since the $^{1,3}E$ states are at higher energy in the Mo and W derivatives, 313- and 366-nm irradiation would give preferential amine loss in these cases, especially since internal conversion in the second- and third-row metals is probably faster due to greater spin–orbit coupling.
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