

ic as well as local diamagnetic contributions. It is probably for this reason that we found the charges did not correlate well with the shift values. Whether or not these same functions also predict other molecular ground state properties reasonably well remains to be investigated. It is anticipated, however, that other properties which depend on all the molecular orbitals collectively will be reasonably well accounted for, whereas properties which are indicative of a portion or all of any one individual such orbital will most likely not fare as well.

It is very informative to also compare, using Table III, the operator moments of the three molecules, $RC_6H_5Cr(CO)_3$, with the moments computed from Mulliken and Lowdin point charges. Recall the above reference to the equal division between AO's χ_i and χ_j of overlap population $2NC_iC_jS_{ij}$ from the Mulliken population analysis and that this is avoided in the Lowdin charge calculation. The numerical results of Table III permit one to conclude that, using the Lowdin charge convergence to arrive at a set of MO coefficients, the values of the moments derived from Lowdin point charges (fourth column of numbers) are much closer to the more difficult to evaluate operator moments (second column of numbers) than are the moments derived from the simple Mulliken point charges. The better agreement derives probably from not having to cope with the quantity $2NC_iC_jS_{ij}$ when using the Lowdin procedure. However, only the order of the operator moments was the same as the order of experimental moments (Table III), so that

even the order of Lowdin point charge moments cannot be relied upon to accurately reflect changes in a series of related molecules.

Finally, it is of chemical interest to point out the computed directions of the operator dipole moments. The direction of the moment of $C_6H_5Cr(CO)_3$ has already been discussed above; *i.e.*, benzene is the positive end and $(CO)_3$ constitutes the negative end of the dipole moment vector, which is directionally coincident with the molecular z axis, or C_3 symmetry axis (Figure 1). For the fluorobenzene derivative, $FC_6H_5Cr(CO)_3$, the resultant, or net moment, of the three moments, u_x , u_y , and u_z , was tilted $\sim 12^\circ$ away from the z axis and toward F and was in the plane which contains F, Cr, and the z axis (Figure 2). On the other hand, it was found for $H_2NC_6H_5Cr(CO)_3$ that the net moment tilted away from the latter's molecular z axis but also away from the NH_2 substituent as can be visualized from Figure 2. These directional results are consistent with the notions that F and NH_2 withdraw and donate electron density, respectively.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the School of Physical and Mathematical Sciences of North Carolina State University for support of this research.

Registry No. $C_6H_5Cr(CO)_3$, 12082-08-5; $H_2NC_6H_5Cr(CO)_3$, 12108-11-1; $FC_6H_5Cr(CO)_3$, 12082-05-2.

Contribution from the Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Photoreactions of Aminepentacarbonylmolybdenum(0) and -tungsten(0) Complexes

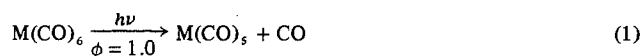
MARK WRIGHTON

Received September 12, 1973

The ligand photosubstitution processes in $M(CO)_5L$ ($M = Mo$ and W ; $L = NH_3$, n -PrNH₂, and piperidine) upon excitation with 366-, 405-, or 436-nm light have been investigated. Photosubstitution of both L and CO is found and the quantum yields are dependent on the excitation wavelength. Photosubstitution of L dominates the chemical decay paths of the excited state with CO substitution becoming more important at shorter excitation wavelengths. Photosubstitution of CO for $M = Mo$ is generally higher than for $M = W$ in the $M(CO)_5L$ complexes investigated. Typical quantum yields for M-L cleavage at 405 nm are of the order of 0.5 as determined by measuring the formation of $M(CO)_6$ by photolysis of $Mo(CO)_5NH_3$ or $W(CO)_5$ (piperidine) in the presence of CO. Substitution yields for CO release are in the range of 10^{-2} – 10^{-1} as determined by photolysis of $M(CO)_5L$ in the presence of excess L yielding $M(CO)_4L_2$ complexes. Importantly, the total reaction quantum yields are less than unity.

Introduction

Metal carbonyls are among the most photosensitive coordination compounds, and for the mononuclear binary carbonyls CO dissociation is thought to account for a large fraction of the excited state chemical decay paths.¹ Included among the most photoreactive metal carbonyls are $Mo(CO)_6$ and $W(CO)_6$ where reaction 1 is measured to occur with unit



$M = Mo$ and W

quantum efficiency as reflected in ultimate formation yields of the substituted product $M(CO)_5L$ when irradiations are

carried out in the presence of a nucleophile, L' .² This procedure has led to an explosion of the number of derivatives of metal carbonyls since the reaction can be carried out at room temperature (or lower), and often high yields of *only* the monsubstituted complex have been obtained. Selective formation of the $M(CO)_5L$ derivative can be aided by running the reaction to small conversion to prevent competitive absorption of light by the product and/or by forming first a relatively nonphotosensitive $M(CO)_5L'$ complex followed by thermal exchange of L' by L. For many situations tetrahydrofuran has served as L' in the synthetic sequence of reactions 1–3.³ The photosensitivity of $M(CO)_5L$ complexes

(1) M. Wrighton, *Chem. Rev.*, in press.

(2) W. Strohmeier and S. von Hobe, *Chem. Ber.*, 94, 761 (1961).
(3) W. Strohmeier, *Angew. Chem.*, 76, 873 (1964).



with respect to loss of CO as reflected in the quantum yields for the formation of $M(CO)_4L_2$, reaction 4, is known to de-



pend both on the ligand, L, and the excitation wavelength.^{4,5} The difference in the quantum yield for reaction 4 and unity is thought to be accounted for by the photodissociation of L from $M(CO)_5L$, reaction 5.^{4,5} For M = W and L = pyridine



the quantum efficiencies of both (4) and (5) were determined with the efficiency decreasing for (5) and increasing for (4) by increasing the excitation energy, but at none of the wavelengths studied did the sum of the yields for reactions 4 and 5 equal unity. By way of contrast, for M = W and Mo and L = amine, it was concluded⁷ that the M-N bond is photostitution inert while the M-C bond is photosubstitution labile leading to $M(CO)_4LL'$ products.

In this report I describe results obtained upon 366-, 405-, and 436-nm photolysis of $M(CO)_5L$ (M = W and Mo; L = NH_3 , *n*-PrNH₂, and piperidine). Both reactions 4 and 5 have been investigated, and the information raises serious doubts regarding the previous thoughts regarding overall reactivity^{4,5} and the relative efficiencies of CO vs. L photodissociation.⁷

Results

(a) **Irradiation of $M(CO)_5L$ in the Presence of L.** Irradiation of $M(CO)_5L$ (M = W and Mo; L = *n*-PrNH₂ and piperidine) in the presence of L gives smooth formation of $M(CO)_4L_2$ products. Reactions were typically carried out in degassed benzene solutions of $\sim 10^{-4}$ M $M(CO)_5L$ and 0.25 M L at 25°. Quantum yields for the formation of $M(CO)_4L_2$ are given in Table I for irradiations using 436-, 405-, and 366-nm wavelength light, and typical uv-vis absorption spectral changes are shown in Figure 1 for the $W(CO)_5(\text{piperidine})$ to $W(CO)_4(\text{piperidine})_2$ conversion. Isosbestic points were obtained and were preserved to greater than 80% conversion evidencing lack of either thermal or further photochemical reaction of the $M(CO)_4L_2$ products. Limiting uv-vis spectra for $M(CO)_4L_2$ are very similar to the electronic spectra of $M(CO)_4(\text{ethylenediamine})$ (M = Cr, Mo, and W)⁸ consistent with a cis-disubstituted product confirmed additionally by the characteristic four-band pattern in the CO stretching region in the ir absorption spectrum. Photoexchange of L in $M(CO)_5L$ is almost certainly occurring (*vide infra*) but is, of course, undetectable since no net chemical change occurs.

Two trends are found for the photoreactivity of $M(CO)_5L$ in the presence of L: (1) the quantum yields increase markedly for $M(CO)_4L_2$ formation upon shorter wavelength excitation, and (2) formation quantum yields for $M(CO)_4L_2$ are substantially larger for M = Mo than for M = W.

(b) **Irradiation of $M(CO)_5L$ in the Presence of X.** Irradi-

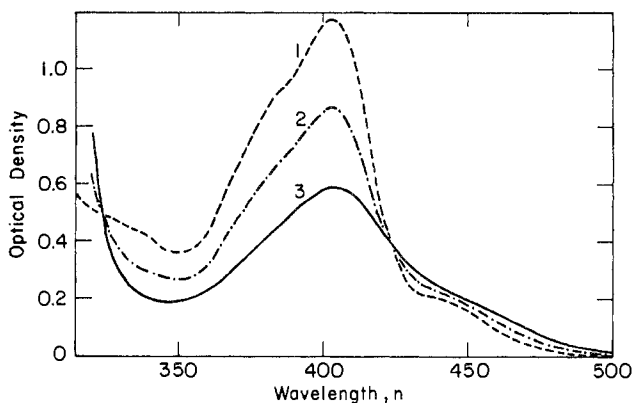


Figure 1. Conversion of $W(CO)_5(\text{piperidine})$ to $W(CO)_4(\text{piperidine})_2$ upon 366-nm ($\sim 10^{-7}$ einstein/min) irradiation in benzene solution, 0.25 M piperidine at 25°. Curve 1 is the zero time spectrum and curves 2 and 3 are spectra after two different irradiation times.

ation of $M(CO)_5L$ (M = W and Mo; L = NH_3 , *n*-PrNH₂, and piperidine) in the presence of an added nucleophile, X, generates $M(CO)_5X$ as the only photoproduct for X = CO (CO exchange would not give any net chemical change) and as the dominant photoproduct for X = 1-pentene. Quantum yields for the substitution reaction are given in Table I for irradiation with 436-, 405-, and 366-nm wavelength light. Typical uv-vis absorption spectral changes for M = W, L = NH_3 , and X = 1-pentene are given in Figure 2 and for M = Mo, L = NH_3 , and X = CO in Figure 3. The $M(CO)_5X$ products were identified by uv-vis and ir absorption spectra by comparisons with authentic samples of the products. The generation of $M(CO)_4(L)(1\text{-pentene})$ was not measured but is an expected photoproduct for X = 1-pentene. Since the $M(CO)_5X$ products absorb very weakly in the region below $25,000\text{ cm}^{-1}$, I have taken the expedient of measuring the disappearance of $M(CO)_5L$ absorption to determine substitution quantum yields. Some ambiguity is introduced, particularly for M = Mo, since CO dissociation should lead to $M(CO)_4LX$ products. It is certain, though, from the results for X = CO that M-L cleavage reaction yields are very high (>0.5), being invariably much larger than for M-CO cleavage. Disappearance yields are only modestly affected by variation in the excitation wavelength, and there is no marked metal dependence.

(c) **Entering Group Concentration Effects.** The possibility of an associative photosubstitution process was tested by irradiation of $W(CO)_5(\text{piperidine})$ in the presence of various concentrations of added piperidine or 1-pentene. Results of the study are summarized in Table II and show that in the range of 0.025–1.0 M added nucleophile the relative quantum yields for either CO substitution or piperidine substitution are independent of the entering group concentration.

(d) **Spectra of the $M(CO)_5L$ Complexes.** The electronic spectra of the $M(CO)_5L$ complexes are all very similar with the major difference being that for M = W a band at 440 nm ($\epsilon \sim 600$) is found while no corresponding transition is seen in the M = Mo case. Each of the $M(CO)_5L$ complexes exhibits a transition in the vicinity of 400 nm ($\epsilon \sim 4500$), and the W complexes exhibit a shoulder on this band at 375 nm. Low-temperature (77°K) spectra in EPA reveal, however, that, in part, the shoulder contains vibrational structure of the 400-nm band, but the band remains asymmetric even at 77°K. The $Mo(CO)_5NH_3$ complex does not exhibit vibrational structure on the 400-nm band at 77° and there is no

(4) W. Strohmeier and D. von Hobe, *Chem. Ber.*, **94**, 2031 (1961).

(5) W. Strohmeier and D. von Hobe, *Z. Phys. Chem. (Frankfurt am Main)*, **34**, 393 (1962).

(6) M. Wrighton, G. S. Hammond, and H. B. Gray, *Mol. Photochem.*, **5**, 179 (1973).

(7) G. Schwenzer, M. Y. Darensbourg, and D. J. Darensbourg, *Inorg. Chem.*, **11**, 1967 (1972).

(8) H. Saito, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jap.*, **41**, 359 (1968).

Table I. Quantum Yields for Photosubstitution of $M(\text{CO})_5\text{L}$ Complexes

| M | L | Entering group, X | Product | $\Phi_{366 \text{ nm}}^a$ | $\Phi_{405 \text{ nm}}^a$ | $\Phi_{436 \text{ nm}}^a$ |
|----|-----------------------------|-----------------------------|------------------------------------|---------------------------|---------------------------|---------------------------|
| Mo | NH_3 | CO | $\text{Mo}(\text{CO})_6$ | | 0.64 | 0.58 |
| W | Piperidine | CO | $\text{W}(\text{CO})_6$ | | 0.65 | |
| Mo | Piperidine | Piperidine | $\text{Mo}(\text{CO})_4\text{L}_2$ | 0.13 | 0.11 | 0.048 |
| Mo | <i>n</i> -PrNH ₂ | <i>n</i> -PrNH ₂ | $\text{Mo}(\text{CO})_4\text{L}_2$ | 0.24 | 0.20 | 0.057 |
| W | Piperidine | Piperidine | $\text{W}(\text{CO})_4\text{L}_2$ | 0.034 | 0.0081 | 0.0061 |
| W | <i>n</i> -PrNH ₂ | <i>n</i> -PrNH ₂ | $\text{W}(\text{CO})_4\text{L}_2$ | 0.057 | 0.022 | 0.016 |
| Mo | NH_3 | 1-Pentene | $\text{Mo}(\text{CO})_5\text{X}^b$ | 0.74 | 0.84 | 0.71 |
| W | NH_3 | 1-Pentene | $\text{W}(\text{CO})_5\text{X}^c$ | 0.49 | 0.66 | 0.56 |
| W | <i>n</i> -PrNH ₂ | 1-Pentene | $\text{W}(\text{CO})_5\text{X}^c$ | 0.60 | 0.65 | 0.73 |
| W | Piperidine | 1-Pentene | $\text{W}(\text{CO})_5\text{X}^c$ | 0.45 | 0.51 | 0.49 |

^a All quantum yields are $\pm 10\%$. ^b Constitutes $>70\%$ of primary photoproducts. ^c Constitutes $>90\%$ of primary photoproducts.

Table II. Entering Group Concentration Effects on Photosubstitution in $\text{W}(\text{CO})_5(\text{piperidine})^a$

| Entering group, M | Product | Irradiation λ , nm | Relative quantum yield ^b |
|-------------------|--|----------------------------|-------------------------------------|
| Piperidine, 0.025 | $\text{W}(\text{CO})_4(\text{piperidine})_2$ | 366 | 1.10 |
| Piperidine, 0.25 | $\text{W}(\text{CO})_4(\text{piperidine})_2$ | 366 | 1.00 |
| Piperidine, 1.00 | $\text{W}(\text{CO})_4(\text{piperidine})_2$ | 366 | 0.98 |
| 1-Pentene, 0.025 | $\text{W}(\text{CO})_5(1\text{-pentene})$ | 436 | 0.94 |
| 1-Pentene, 0.25 | $\text{W}(\text{CO})_5(1\text{-pentene})$ | 436 | 1.00 |
| 1-Pentene, 1.00 | $\text{W}(\text{CO})_5(1\text{-pentene})$ | 436 | 1.09 |

^a Irradiation in degassed benzene solution at 25° . ^b Relative yields are $\pm 10\%$.

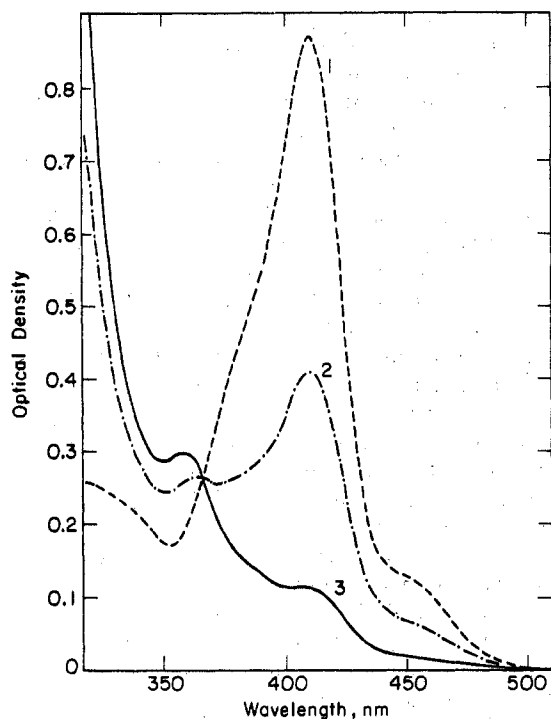


Figure 2. Conversion of $\text{W}(\text{CO})_5(\text{NH}_3)$ to $\text{W}(\text{CO})_5(1\text{-pentene})$ upon 436-nm ($\sim 10^{-7}$ einstein/min) irradiation in benzene solution, 0.25 M 1-pentene at 25° . Curve 1 is the zero time spectrum and curves 2 and 3 are spectra after two different irradiation times.

pronounced asymmetry. All of the complexes exhibit relatively weak absorptions in the vicinity of 340 nm which probably tail considerably. Typical 298°K spectra of $M(\text{CO})_5\text{L}$ can be found in Figures 1-3 and representative 77°K spectra are shown in Figure 4. Band maxima and molar extinction coefficients for the lowest energy absorptions in $M(\text{CO})_5\text{L}$ are detailed in Table III. A small, but definite, shift to higher energy is found for the L having the more alkyl substituents on the donor nitrogen atom for both M =

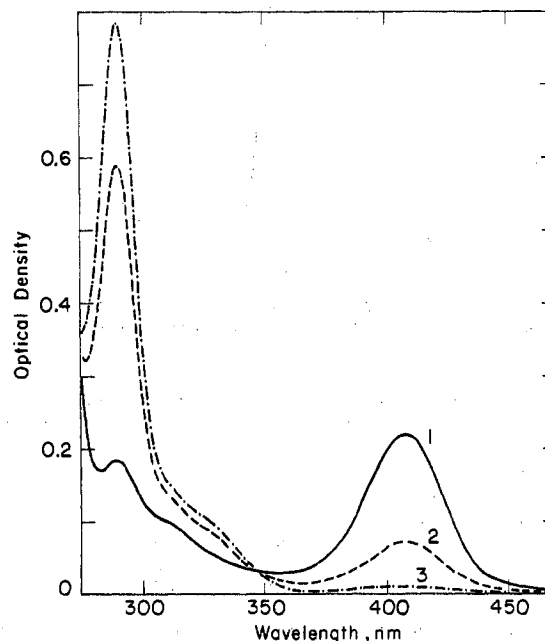


Figure 3. Conversion of $\text{Mo}(\text{CO})_5(\text{NH}_3)$ to $\text{Mo}(\text{CO})_6$ upon 436-nm ($\sim 10^{-7}$ einstein/min) irradiation in continuously CO purged isoctane solution at 25° . Curve 1 is the zero time spectrum and curves 2 and 3 are spectra after two different irradiation times.

Mo and W, and generally the Mo complexes exhibit the first room-temperature maximum at slightly higher energies than the corresponding W species.

Discussion

The results allow some important conclusions to be made regarding the excited state decay paths in the $M(\text{CO})_5\text{L}$ complexes. Wavelength-dependent quantum yields, overall reaction quantum yields, and the effect of the central metal will be discussed.

First, we need to consider the types of excited states accessible at the irradiation wavelengths of 366-, 405-, and 436-nm. Evidence has been presented^{6,9} for associating the 440-nm band with the spin-forbidden $^1A_1(e^4b_2^2) \rightarrow ^3E(e^3b_2^2a_1^1)$ ligand field (LF) transition. The 400-nm band was assigned^{6,8,9} as the corresponding spin-allowed $^1A_1(e^4b_2^2) \rightarrow ^1E(e^3b_2^2a_1^1)$ absorption. Our results indicate that the shoulder at ~ 375 nm in the $\text{W}(\text{CO})_5\text{L}$ complexes is partially attributable to the vibrational structure of the $^1A_1 \rightarrow ^1E$ absorption. Asymmetry of the band, though, suggests some contribution from the spin-forbidden $^1A_1(e^4b_2^2) \rightarrow ^3A_2(e^4b_2^1b_1^1)$ transition.¹⁰ The band is not present in the corresponding Mo systems and is thus assigned as spin forbidden. Tail absorption by the set of bands near

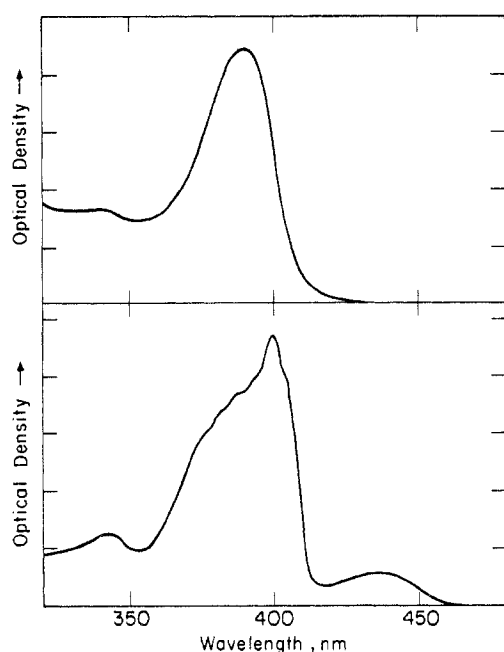


Figure 4. Comparison of uv-vis absorption spectra of $\text{Mo}(\text{CO})_5(\text{NH}_3)$ (upper curve) and $\text{W}(\text{CO})_5(\text{NHC}_5\text{H}_{10})$ (lower curve) in EPA at 77°K.

Table III. Electronic Spectral Features of $\text{M}(\text{CO})_5\text{L}$ Complexes

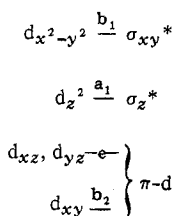
| M | L | Band max, nm (ϵ) ^a |
|----|-----------------------------|--|
| Mo | NH_3 | 399 (4200) |
| Mo | <i>n</i> -PrNH ₂ | 396 (4200) |
| Mo | $\text{NHC}_5\text{H}_{10}$ | 394 (5000) |
| W | NH_3 | 408 (3800); 440 (600) sh |
| W | <i>n</i> -PrNH ₂ | 406 (440); 440 (610) sh |
| W | $\text{NHC}_5\text{H}_{10}$ | 403 (3850); 440 (590) sh |

^a Benzene solution at 25°; sh denotes a shoulder. Band positions are ± 1 nm for the ~ 400 -nm maximum and ± 5 nm for the ~ 440 -nm shoulder. Molar extinction coefficients are $\pm 10\%$.

340 nm in the $\text{W}(\text{CO})_5\text{L}$ complexes is likely at energies as low as 366 nm. The weak transitions near 340 nm can be associated with LF absorption featuring population of the b_1 (σ_{xy}^*) orbital including principally the orbitally forbidden, spin-allowed ${}^1\text{A}_1(e^4b_2^2) \rightarrow {}^1\text{A}_2(e^4b_2^1b_1^1)$ transition.¹⁰

Turning now to reactivity we can use the model recently outlined¹¹ to rationalize LF excited state substitution behavior. The lack of substantial entering group concentration effects on substitution quantum yields is consistent with a dissociative type mechanism for photosubstitution of either CO or L in $\text{M}(\text{CO})_5\text{L}$. In these approximately C_{4v} $\text{M}(\text{CO})_5\text{L}$ situations the scheme proposed⁶ for $\text{W}(\text{CO})_5(\text{pyridine})$ serves nicely, Scheme I. The two types of one-electron excitations

Scheme I



(10) A detailed treatment of the electronic spectra of C_{4v} , d^6 metal carbonyls is to be reported elsewhere, but the basis for this argument is to be found in (a) V. M. Miskowski, Ph.D. Thesis, California Institute of Technology, 1973; (b) G. L. Geoffroy, M. S. Wrighton, G. S. Hammond, and H. B. Gray, *Inorg. Chem.*, **13**, 430 (1974); (c) A. D. Wentworth and T. S. Piper, *ibid.*, **4**, 709 (1965).

accessible, $(e^4b_2^2) \rightarrow (e^3b_2^2a_1^1)$ and $(e^4b_2^2) \rightarrow (e^4b_2^1b_1^1)$, result in strong σ -antibonding effects along the z and x,y axes, respectively. Since most of the chemical action occurs from the lowest excited state (population of σ_z^*) z -axis (OC-M-amine) labilization is consistent with the model and, thus, a general rationale of efficient M-amine cleavage is provided. Increasing substitution of CO at shorter irradiation wavelengths is consistent with equatorial CO labilization due to strong σ -antibonding effects along the x,y axes in the ${}^{1,3}\text{A}_2$ excited states which are achieved by higher energy excitation. Competitive internal conversion from the ${}^{1,3}\text{A}_2$ to the ${}^{1,3}\text{E}$ excited states is an attractive pathway to account for high yields of M-amine cleavage upon high energy excitation. The model¹¹ also predicts that population of σ_z^* should labilize the axial CO. The fact that some disubstituted product is formed upon 436-nm excitation is consistent with dissociation of an axial CO from $\text{M}(\text{CO})_5\text{L}$ with rearrangement leading to a cis-disubstituted product in the presence of L. The fact that the quantum yields for amine dissociation overwhelm those for axial CO release is likely due in part to the fact that any labilization of the axial CO by electronic excitation cannot lead to larger absolute rate constants for dissociation than for the M-amine bond which is much more labile in the ground state and also undergoes further labilization upon population of σ_z^* . Since the ${}^{1,3}\text{A}_2$ states yield equatorial CO labilization and the ${}^{1,3}\text{E}$ states give axial CO labilization by the model, the stereochemistry of CO dissociation should be wavelength dependent in addition to the now established fact that CO dissociation quantum yields are wavelength dependent.

Interestingly, the quantum yields for CO release in the $\text{Mo}(\text{CO})_5\text{L}$ complexes are consistently greater than for the corresponding W species. This is particularly true for the 436-nm irradiations. This trend is significant since the M-amine thermal dissociation rates are much larger for the Mo than for the W complexes. Earlier work has shown that for a given M the quantum yield for CO substitution in $\text{M}(\text{CO})_5\text{L}$ increased with increased M-L bond strength.^{4,5} One attractive possibility to account for the metal dependence of CO substitution quantum yields is to invoke different reactivity for the ${}^1\text{E}$ and ${}^3\text{E}$ excited states. This suggestion has some credibility since we already know that reactions from upper electronically excited states are possible, and from the absorption spectra triplets are not populated directly in the Mo as they are in the W complexes. Nor do the $\text{Mo}(\text{CO})_5\text{L}$ complexes undergo radiative decay while the W analogs all yield ${}^3\text{E} \rightarrow {}^1\text{A}_1$ luminescence.⁹ Triplet sensitization experiments could, in principle, serve as a test for the differing reactivity of the ${}^1\text{E}$ and ${}^3\text{E}$, but fundamental questions surrounding efficiency of triplet excitation to metal containing molecules remain unanswered and are currently under investigation in our laboratory. In the only reported information,¹² $\text{Cr}(\text{CO})_6$ undergoes triplet sensitized substitution with the same quantum efficiency as in direct irradiation. Differences in reactivity for LF states of the same configuration but of different multiplicity cannot be accounted for by either the Wrighton, Gray, and Hammond model¹¹ or Zink's model¹³ for substitutional reactivity of LF excited states. Differences in the degree of configuration interaction do not account for the metal dependence since the LF parameters

(11) M. Wrighton, H. B. Gray, and G. S. Hammond, *Mol. Photochem.*, **5**, 165 (1973).

(12) A. Vogler, *Z. Naturforsch. B*, **25**, 1069 (1970).

(13) (a) J. I. Zink, *J. Amer. Chem. Soc.*, **94**, 8039 (1972); (b) *Inorg. Chem.*, **12**, 1018 (1973); (c) *Mol. Photochem.*, **5**, 151 (1973); (d) *Inorg. Chem.*, **12**, 1957 (1973).

for W and Mo appear to be very similar. A more conservative rationale of the metal dependence is simply to associate different absolute dissociation rate constants with the subtle differences in the degree of π vs. σ bonding of CO in the Mo and W systems, which is thought to give rise to the similar LF parameters for Cr, Mo, and W.¹⁴ Changes of this type could account for the observations within the framework of the models for LF reactivity.^{11,13}

The overall photosubstitution quantum yields are less than unity. This fact is in contrast to the commonly held belief that the sum of the quantum yields for reactions 4 and 5 is unity. Two likely mechanisms for the inefficiency are (1) lack of completely efficient cage escape of the extruded ligand and the coordinatively unsaturated complex and/or (2) nonchemical nonradiative decay directly to the ground state from the electronically excited $M(CO)_5L$. Although the data are not definitive, the following points can be made. First, the quantum yield for substitution seems essentially the same when the entering group molecules are at sufficiently high concentration to constitute a large fraction of any solvent cage. This fact tends to support the notion that nonchemical nonradiative decay accounts for a substantial fraction of the inefficiency. The lack of any photosubstitution of pyridine in $W(CO)_5(\text{pyridine})$ in a neat 1-pentene glass at 77°K, with emission and nonchemical nonradiative decay the only decay processes observed,⁶ is consistent with initial population of a bound state which requires some thermal activation to achieve a dissociative reaction. Nonradiative nonchemical decay from the initially achieved bound state is thus possible. Experiments are now in progress to assess the importance of cage effects in photosubstitution reactions.

The relative importance of M-amine vs. M-CO photosubstitution found in this work is substantially different from that reported by other workers. The quantum yield data in this paper accurately reflect *primary photoprocesses* which are measured in a time scale during which thermal processes are unimportant. Further, the experiments have been carried out in benzene or isooctane compared to tetrahydrofuran⁷ and solvent effects are known to affect ultimate product yields.^{4,5} The possibility of reversal of relative importance of primary photodissociations by solvents merits further investigation.

Summary

Both CO and L substitution occur in $M(CO)_5L$ complexes upon irradiation in the 366–436-nm region. Dissociative mechanisms obtain, and M-L cleavage, not M-CO cleavage, dominates the chemical decay paths in all cases studied. The substitution of L occurs largely *via* population of the $a_1(\sigma_x^*)$ orbital, while increasing yields of CO substitution obtain upon population of a higher LF state featuring population of the $b_1(\sigma_{xy}^*)$ orbital.

(14) N. A. Beach and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 5713 (1968).

Experimental Section

Preparation of $M(CO)_5L$. The $M(CO)_5L$ complexes were prepared by near-uv irradiation of $M(CO)_6$ in the presence of L^3 in aliphatic hydrocarbon 25° solutions purged continuously with N_2 or degassed by three freeze-pump-thaw cycles. For $L = NH_3$, N_2 was not used but NH_3 was bubbled vigorously through the solution. The $M(CO)_5NH_3$ complexes are only sparingly soluble in aliphatic hydrocarbon solution and precipitated from the reaction mixture. The precipitate was collected by filtration and washed several times with the hydrocarbon solvent to remove any $M(CO)_6$ and dried in air. The $M(CO)_5NH_3$ were identified by ir and uv-vis spectra.¹⁵ For $W(CO)_5L$ ($L = n\text{-PrNH}_2$ and piperidine) the reaction mixture was concentrated by rotary evaporation and then chromatographed in the dark on neutral Woelm alumina. Elution was first with isooctane until no $W(CO)_6$ could be detected in the eluant (by uv absorption). The $W(CO)_5L$ moves quickly down the column by eluting with diethyl ether. The diethyl ether solution of $W(CO)_5L$ was evaporated to dryness and the crystals collected. Ir and uv-vis spectra confirmed the purity of the $W(CO)_5L$ complexes. The $Mo(CO)_5L$ ($L = n\text{-PrNH}_2$ and piperidine) were not isolated but prepared in solution by short irradiation of mixtures of $Mo(CO)_6$ and 0.25 M L. The $M(CO)_5L$ was the only product formed as evidence by the preservation of isosbestic points in the $M(CO)_6 \rightarrow M(CO)_5L$ conversion followed by uv-vis absorption spectral changes.

Irradiation Procedure. Three-milliliter aliquots of benzene solutions of $M(CO)_5L$ ($\sim 10^{-4}$ M) and an added nucleophile ($n\text{-PrNH}_2$, HNC_3H_7 , or 1-pentene) at 0.025–1.0 M were placed in Pyrex 13 × 100 mm test tubes with constrictions and degassed by three freeze-pump-thaw cycles and hermetically sealed. Irradiation sources were either 450 or 550 W Hanovia medium pressure Hg lamps filtered with appropriate Corning glass filters to isolate the 436-, 405-, and 366-nm wavelength light. The samples were irradiated in merry-go-rounds¹⁶ and ferrioxalate actinometry¹⁷ was used to measure the light intensities which were of the order of 1×10^{-7} einstein/min. For irradiation in the presence of CO, open test tubes were used and isooctane solutions of $M(CO)_5L$ were purged continuously with CO. Irradiation was carried out in a fixed position and light intensity measured immediately after reaction was complete. All reactions were analyzed quantitatively by measuring the decline of uv-vis absorption at 400 nm after the primary product had been identified by ir and uv-vis spectra. The $M(CO)_5L$ solutions undergo little or no thermal reaction in the time required for the photolysis.

Electronic Spectra. All spectra were measured using a Cary 17 absorption spectrophotometer. For measurements at 77°K a quartz dewar with optical flats for windows was used and the EPA (from MCB Chemicals) solution was placed in a round quartz cell placed in direct contact with liquid N_2 .

Acknowledgment. I thank the National Science Foundation for support of this research.

Registry No. $Mo(CO)_5NH_3$, 15388-22-4; $W(CO)_5(\text{piperidine})$, 31082-68-5; $Mo(CO)_5(\text{piperidine})$, 19456-57-6; $Mo(CO)_5(n\text{-PrNH}_2)$, 15228-33-8; $W(CO)_5(n\text{-PrNH}_2)$, 15228-29-2; $W(CO)_5NH_3$, 15133-64-9; CO, 630-08-0; piperidine, 110-89-4; $n\text{-PrNH}_2$, 107-10-8; 1-pentene, 109-67-1.

(15) Ir and uv-vis spectroscopic data for $M(CO)_5L$ complexes are found in ref 1, 6–9, and 14 and in "Organic Synthesis via Metal Carbonyls," Vol. I, I. Wender and P. Pino, Ed., Interscience, New York, N. Y., 1968, pp 170–177.

(16) F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, **1**, 245 (1969).

(17) (a) C. A. Parker, *Proc. Roy. Soc., Ser. A*, **220**, 104 (1953); (b) C. G. Hatchard and C. A. Parker, *ibid.*, **235** 518 (1956).