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Interpretation of the Electronic Spectra of Low-Spin d^6 $M(\text{CO})_5\text{X}$ Complexes. Primary Excited State Decay Paths in $\text{Re}(\text{CO})_5\text{X}$ Complexes

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Abstract: The electronic spectra of $\text{Re}(\text{CO})_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), $[\text{M}(\text{CO})_5\text{NH}_2\text{CH}_3]\text{Cl}$ ($\text{M} = \text{Mn}, \text{Re}$), and $[(\text{C}_2\text{H}_5)_4\text{N}][\text{M}(\text{CO})_5\text{Br}]$ ($\text{M} = \text{Cr}, \text{W}$) have been measured. The emission spectra and photochemistry of the $\text{Re}(\text{CO})_5\text{X}$ complexes have also been investigated. The new electronic spectral studies along with data in the literature allow definitive assignment of the lowest absorptions as ligand field (LF) ${}^1\text{A}_1(\text{e}^4\text{b}_2^2) \rightarrow {}^1,3\text{E}(\text{e}^3\text{b}_2^2\text{a}_1^1)$ for a large class of low-spin d^6 $\text{M}(\text{CO})_5\text{X}$ complexes. Emission from $\text{Re}(\text{CO})_5\text{X}$ occurs from the ${}^3\text{E}(\text{e}^3\text{b}_2^2\text{a}_1^1)$ state and is strongly dependent on temperature in the range 20–100 K. Quantitative emission measurements have been made for the pure solids. Photochemistry of $\text{Re}(\text{CO})_5\text{X}$ at 298 K involves substitution of CO with a quantum yield of up to 0.76 depending on X and the excitation wavelength. The observed chemistry and variable quantum yields accord well with the electronic nature of the lowest excited states.

Compelling spectroscopic^{1–4} and photochemical^{5–8} evidence supports the assignment of ligand field (LF) ${}^1,3\text{E}(\text{e}^3\text{b}_2^2\text{a}_1^1)$ to the lowest excited states in low-spin d^6 $\text{M}(\text{CN})_5\text{X}^{n-}$ and $\text{M}(\text{NH}_3)_5\text{X}^{n+}$ ($\text{M} = \text{Co(III)}, \text{Rh(III)}, \text{Ir(III)}$; $\text{X} = \pi$ -donor, σ -donor) complexes. In these cases the energetic separation of the $d\sigma^*$ orbitals, $d_{x^2-y^2}(b_1)$ and $d_{z^2}(a_1)$, is relatively large. Thus, the lowest excited states involve population of one or the other of these orbitals with very little mixing via configuration interaction. Population of $d_{z^2}(a_1)$ increases the substitution lability of the ligands on the z axis, and population of $d_{x^2-y^2}(b_1)$ labilizes the ligands on the x and y axes due to the directed σ -antibonding character of these orbitals.^{9,10}

The electronic spectroscopy¹¹ and photosubstitution chemistry^{12,13} of a series of $\text{M}(\text{CO})_5\text{X}$ ($\text{X} = n$ -electron donor; $\text{M} = \text{Mo}, \text{W}$) complexes, also of the d^6 low-spin electronic configuration, have been interpreted successfully by assigning the lowest excited states as ${}^1,3\text{E}(\text{e}^3\text{b}_2^2\text{a}_1^1)$.^{11–13} Such an interpretation follows from the LF assignment¹⁴ of lowest excited states in the d^6 $\text{M}(\text{CO})_6$ species and the recognition that X is weaker in LF strength than CO. Recently, an extensive account of the electronic spectra of d^6 , pentacarbonylhalogenometal complexes has appeared¹⁵ where the ${}^1\text{A}_1(\text{e}^4\text{b}_2^2) \rightarrow {}^1\text{E}(\text{e}^3\text{b}_2^2\text{a}_1^1)$ interpretation was generally adopted. The matrix isolated $\text{M}(\text{CO})_5$ ($\text{Cr}, \text{Mo}, \text{W}$) species have also been investigated,¹⁶ and polarized spectral measurements^{16b} of $\text{Cr}(\text{CO})_5$ are in accord with the ${}^1\text{A}_1(\text{e}^4\text{b}_2^2) \rightarrow {}^1\text{E}(\text{e}^3\text{b}_2^2\text{a}_1^1)$ assignment for the lowest absorption band.

For *cis*- $\text{M}(\text{CO})_4\text{X}_2$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{X} = \text{aliphatic amine}$) a LF assignment has also been given¹⁷ for the lowest absorption bands. These complexes fall in the category *cis*- ML_4X_2 ,¹⁸ with $\text{X} \ll \text{L}$ in LF strength as does *cis*- $\text{Co}(\text{CN})_4(\text{ethylenediamine})^-$, whose absorption spectrum has also been interpreted in this way.¹⁹

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In the d^6 $\text{Mn}(\text{CO})_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$)²⁰ and corresponding Re complexes,²¹ photoelectron spectra (PES) have revealed that the highest occupied orbital is one of e symmetry and principally halogen in character. Such PES data have influenced Blakney and Allen to assign²² the lowest absorption bands in $\text{Mn}(\text{CO})_5\text{X}$ as charge-transfer (CT) transitions involving depopulation of the highest occupied e level and population of a low lying orbital associated with mainly the carbonyl ligands. Several other investigators²³ have also regarded the lowest absorptions in $\text{M}(\text{CO})_5\text{X}$ as involving CT excitation to the carbonyl groups. An account of the magnetic circular dichroism of $\text{Mn}(\text{CO})_5\text{Br}$ has also recently appeared,²⁴ and the data were interpreted as consistent with an $e(\text{Br}) \rightarrow d_{z^2}$ CT lowest energy transition.

The aim of this paper is to examine critically all available electronic spectroscopic data on d^6 $\text{M}(\text{CO})_5\text{X}$ complexes and also to report some new observations concerning $\text{Re}(\text{CO})_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), $[\text{M}(\text{CO})_5\text{NH}_2\text{CH}_3]\text{Cl}$ ($\text{M} = \text{Mn}, \text{Re}$), and $[(\text{C}_2\text{H}_5)_4\text{N}][\text{M}(\text{CO})_5\text{X}]$ ($\text{M} = \text{Cr}, \text{W}$; $\text{X} = \text{Br}$). Absorption spectra for all of the complexes are reported, and emission spectral and photochemical studies have been carried out for $\text{Re}(\text{CO})_5\text{X}$. These new data now allow definitive discussion of the electronic structure of the d^6 $\text{M}(\text{CO})_5\text{X}$ complexes.

Results

a. Absorption Spectra. The absorption spectra of $\text{Re}(\text{CO})_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), $[\text{M}(\text{CO})_5\text{NH}_2\text{CH}_3]^+$ ($\text{M} = \text{Mn}, \text{Re}$), $\text{W}(\text{CO})_5\text{NH}_3$, and $[\text{M}(\text{CO})_5\text{Br}]^-$ ($\text{M} = \text{Cr}, \text{W}$) have been measured. Electronic absorption spectral data for these complexes along with pertinent data from the literature^{11–14,22} for other d^6 metal carbonyls are summarized in Table I. Figures 1, 2, and 3 show the spectra of some complexes investigated here. The Re and W complexes have remarkably similar spectra except for positions of the bands. The lowest absorption, band I, for these C_{4v} , d^6 Re carbon-

Table I. Electronic Absorption Bands in d⁶ Metal Carbonyls

A. C _{4v} Complexes		Bands, kK (ε) ^a				
Compound	Solvent	Band I	Band II	Band III	Band IV	Band V
[Re(CO) ₅ NH ₂ CH ₃]Cl	EtOH	31.45 (1250)	34.13 (sh) 35.34 (3270)	—	—	42.55 (sh) 37.17 (55 600)
Re(CO) ₅ Cl	EPA	29.07 (750)	31.06 (1940)	~33.0 (~1300)	36.36 (1600) 37.45 (1600)	Not recorded —
	CH ₃ CN	29.33 (0.22)	31.55 (0.693)	~33.7 (0.38)	~37.04 (0.45)	Not recorded
	EtOH	29.24 (0.03)	31.45 (0.10)	~33.9 (0.06)	~37.0 (0.08)	~44.4 (0.70) ~48.08 (1.80)
	Isooctane	28.74 (0.13)	30.77 (0.36)	~32.8 (0.21)	~36.1 (0.29) ~37.2 (0.29)	42.92 (1.330) 47.17 (5.10)
Re(CO) ₅ Br	EPA	28.33 (600)	30.67 (1780)	~32.6 (~1300)	~36.4 (~2400)	Not recorded
	Isooctane	27.93 (0.17)	30.21 (0.48)	~32.3 (0.28)	Not recorded	Not recorded
	EtOH	28.73 (0.03)	30.95 (0.09)	~33.1 (0.05)	~37.0 (0.08)	~42.19 (0.26) 46.51 (1.60)
Re(CO) ₅ I	EPA	26.18 (220)	29.59 (2150)	~31.7 (~1200)	~34.5 (~2400) ~37.0 (~3200)	Not recorded
	CH ₂ Cl ₂	26.24 (0.11)	29.67 (0.99)	~31.6 (0.5)	~35.7 (1.12)	Not recorded
	EtOH	26.81 (215)	29.76 (2000)	~32.1 (940)	~35.1 (2000)	~46.9 (~35 000)
	Isooctane	26.04 (0.02)	28.99 (0.30)	30.77 (0.18)	~36.6 (2800) ~34.1 (0.27) ~36.0 (0.33)	~49.5 (60 000) 40.32 sh (0.70) 44.84 sh (4.20) 47.85 (7.15)
[Mn(CO) ₅ NH ₂ CH ₃] [PF ₆]	EtOH	Not observed	29.41 (—)	—	~37.0 (—)	>50.00
	CH ₂ Cl ₂	Not observed	29.59 (1420)	—	37.0 (sh, 3730)	—
[Mn(CO) ₅ NH ₂ CH ₃]Cl	EtOH	Not observed	29.67 (—)	—	~37.0	—
	EPA	Not observed	29.41 (1200)	—	37.0 (sh, 3100)	—
Mn(CO) ₅ Cl ^b	Cyclohexane	Not observed	26.67 (0.01)	—	—	44.05 (0.5) 50.50 (0.6)
	CH ₃ OH	Not observed	26.52 (600)	—	~37.0 (~1500)	45.05 (13 000) >52.60
Mn(CO) ₅ Br ^b	Cyclohexane	Not observed	25.94 (0.02)	—	~37.0 (0.07)	43.01 (0.45) ~50.00 (0.2) 53.00 (0.75)
	CH ₃ OH	Not observed	26.07 (420)	—	37.0 (1700)	43.95 (15 000) 50.50 (7000)
Mn(CO) ₅ I ^b	Cyclohexane	Not observed	23.53 (380)	32.80 (2310)	—	42.90 (15 300) 50.80 (79 000)
	CH ₃ OH	Not observed	25.00 (360)	33.60 (3000)	36.40 (1500)	42.70 (20 000) 52.63 (88 000)
W(CO) ₅ NH ₃	EtOH	22.73 (0.01)	24.88 (0.06)	~30.8 (0.015)	34.60 (0.035)	40.49 (1.29) ~43.48 (0.76) ~46.08 (0.60)
	EPA	22.73 (0.09)	24.81 (0.39)	30.5 (0.27)	~33.1 (0.33) 34.72 (0.41)	Not recorded
	Benzene	22.73 (600)	24.50 (3800)	Not recorded	Not recorded	—
	Isooctane	21.88 (0.11)	24.04 (0.90)	30.8 (0.31)	33.3 (0.45) 34.60 (0.55)	41.32 (12.0) 43.86 (10.2) 47.17 (6.1)
[W(CO) ₅ Br] ⁻	EtOH	22.03 (500)	24.15 (2230)	30.3 (980)	33.1 (2000) 34.7 (2700)	40.49 (54 000) 43.86 (31 7000) 46.51 (29 000)
	EPA	21.74 (0.05)	24.15 (0.28)	30.3 (0.21)	33.1 (0.30) 34.7 (0.39)	Not recorded
Mo(CO) ₅ NH ₃ ^c	EPA	Not observed	25.64 (0.44)	30.3 (0.16)	Not recorded	Not recorded
	Benzene	Not observed	25.06 (4200)	—	—	—
[Cr(CO) ₅ Br] ⁻	CHCl ₃	Not observed	22.90 (1100)	Not observed	37.0 (10,000)	Not recorded
Cr(CO) ₅ (piperidine) ^c	Alkane	Not observed	23.81 (3500)	—	—	—

B. O _h Complexes in CH ₃ CN ^d		Bands, kK (ε) ^a		
Compound	¹ A _{1g} → ³ T _{1g}	¹ A _{1g} → ¹ T _{1g}	¹ A _{1g} → ¹ T _{2g}	M → CO CT
[Re(CO) ₆] [AlCl ₄]	36.85 (708)	38.50 (1500) 40.70 (2900)	47.10 (4600)	44.50 (20 000) 51.20 (77 900)
[Mn(CO) ₆] [BF ₄]	Not observed	~33.25 (600)?	37.30 (1100)? 39.60 (2200)?	44.50 (16 000) 49.90 (27 000)
W(CO) ₆	28.30 (1000)	29.95 (1680)	37.10 (7400)	34.65 (17 600)
		31.85 (3250)	—	39.55 (9600)
		—	—	43.75 (208 000)
		—	—	46.35 (53 160)
Mo(CO) ₆	28.85 (350)	30.95 (2820)	37.20 (7900)	49.00 (20 060)
		30.15 (1690)	—	34.60 (16 800)
		—	—	42.80 (138 000)
Cr(CO) ₆	Not observed	29.50 (700)	38.85 (3500)	46.50 (23 700)
		31.55 (2670)	—	35.70 (13 100) 43.60 (85 100)

^a Values in parentheses which are italic are the relative absorptivities at an unspecified concentration of the particular complex; all data are for 300 K unless noted otherwise. ^b Reference 22. ^c Reference 11 and 13. ^d Reference 14.

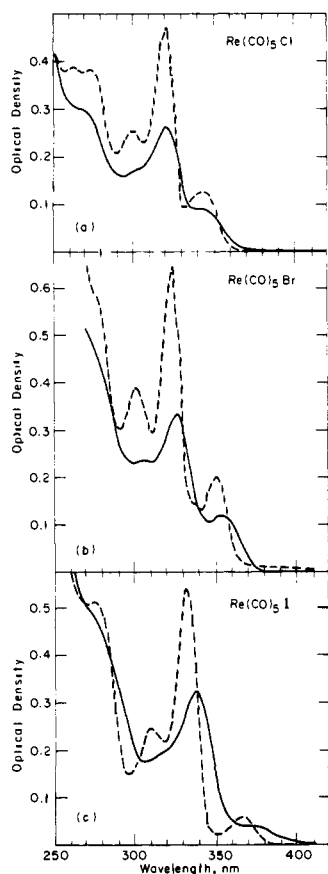


Figure 1. Absorption spectra of $\text{Re}(\text{CO})_5\text{X}$ at 298 K (—) and 77 K (---) in EPA. Molar absorptivities and band positions are given in Table I.

yls usually appears as a shoulder (ϵ 200–1200 $\text{l. mol}^{-1} \text{cm}^{-1}$) at 298 K but becomes better resolved upon cooling to low temperature. The second absorption, band II (ϵ (2–5) $\times 10^3 \text{ l. mol}^{-1} \text{cm}^{-1}$), is the prominent feature of the low energy region of the electronic absorption spectra, and in some cases we find that this band exhibits structure upon cooling the samples to 77 K or lower. This structure is attributable to vibrational excitation, and the maxima appearing on band II are given in Table II for 25 K measurements. The splittings are of the order of 400 cm^{-1} , but the error is rather large, especially for $\text{Re}(\text{CO})_5\text{Br}$ and $\text{Re}(\text{CO})_5\text{Cl}$. No vibrational structure could be resolved for $\text{Re}(\text{CO})_5\text{I}$ even at 25 K. Band III generally appears near the absorption minimum on the high energy side of band II, and band III becomes much better resolved upon cooling to low temperature. For the W complexes band III appears to be resolved into two components at low temperature. The final absorption in the low energy region, band IV, appears to consist of two components which become better resolved at low temperatures. The intensity of band IV is difficult to assess, as it generally appears on the tail of a much more intense absorption which we associate with the onset of band V. The high energy band V consists of several intense ($\epsilon > 10^4 \text{ l. mol}^{-1} \text{cm}^{-1}$) components. We have included data^{11–14,22} for $\text{Mn}(\text{CO})_5\text{X}$ (X = Cl, Br, I), $\text{Cr}(\text{CO})_5(\text{amine})$, and $\text{Mo}(\text{CO})_5\text{NH}_3$ in Table I. The band systems for these complexes follow the same general pattern as found here and are categorized accordingly.

Several important trends are worth noting. For all of the C_{4v} complexes studied the lowest absorption band position is dependent on the unique ligand being consistently ordered: amine > Cl > Br > I. The metal dependence is Re > Mn > W > Cr for a given set of ligands. Bands I and II are

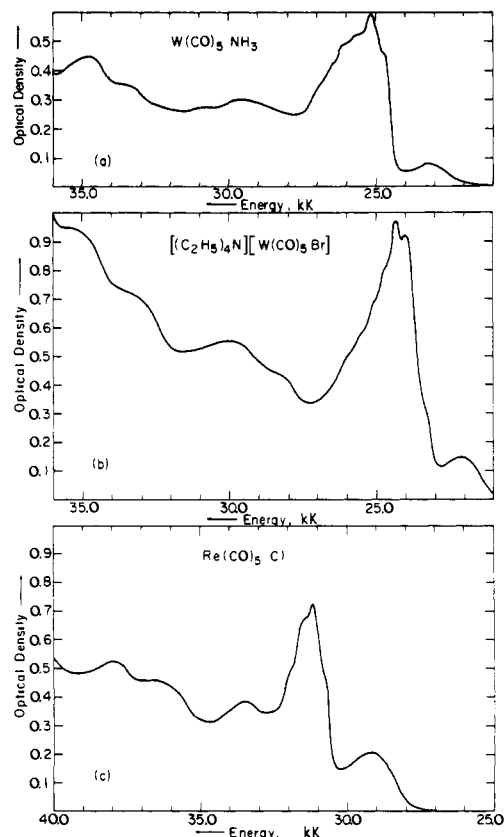


Figure 2. Absorption spectra at 25 K in EtOH using the procedure outlined in the Experimental Section; cf. also Table I for 298 K band positions and intensities.

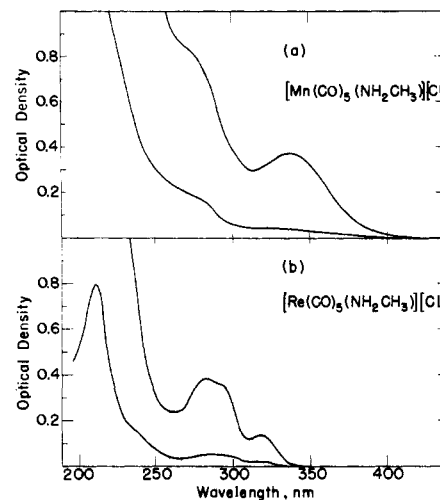


Figure 3. Absorption spectra at 298 K in 1-cm path length cells in EtOH solvent. The curve showing a lower optical density is a diluted sample. Molar absorptivities are given in Table I.

generally substantially red-shifted from the first absorptions¹⁴ in the corresponding O_h $\text{M}(\text{CO})_6$ or $\text{M}(\text{CO})_6^+$. The solvent effects on the positions of the lowest bands for the C_{4v} complexes are small and are generally such that more polar solvents yield higher energy absorptions. The only apparent exception among all of the complexes is $\text{Mn}(\text{CO})_5\text{Cl}$ which is very substitution labile²² at 298 K and may have undergone some conversion to $\text{ClMn}(\text{CO})_n(\text{CH}_3\text{OH})_{5-n}$ in pure CH_3OH .

b. Luminescence Phenomena. The $\text{Re}(\text{CO})_5\text{X}$ complexes as pure solids exhibit luminescence upon near-uv excitation at low temperatures. Corrected emission spectra for the

Table II. Vibrational Structure of Band 11^a

Compound	Band, cm ⁻¹	$\Delta(\nu^n - \nu^{n+1}),$ cm ⁻¹
Re(CO) ₅ Cl	30 817	384
	31 201	375
	31 576	363
	31 949	
Re(CO) ₅ Br	30 581	379
	30 960	388
	31 348	
W(CO) ₅ NH ₃	24 720	430
	25 150	520
	25 670	450
	26 120	380
	26 500	380
[W(CO) ₅ Br] ⁻	26 880	
	23 350	600
	23 950	330
	24 280	410
	24 690	390
	25 080	440
	25 520	480
	26 000	

^aEPA solution at 25 K.

Re(CO)₅X complexes are shown in Figure 4. The structureless emission band overlaps the lowest absorption band to a small extent, but the emission bandwidth at half-height is substantially larger than that for the lowest absorption band in solution. Absorption spectra of thin films of pure Re(CO)₅Cl deposited on quartz flats by evaporation of CH₂Cl₂ solutions show bandwidths and positions very comparable to those found for solutions. While no detailed luminescence measurements for solutions have been made, we note that no emission could be detected at 77 K in EPA even for Re(CO)₅I. Below 77 K the glassy EPA often shatters complicating the interpretation of the emission. Other glassy media were tried, but proved unreliable substantially below 77 K. No luminescence could be detected from Mn(CO)₅Cl at 25 K as a pure solid.

Quantitative luminescence measurements for the pure solids of Re(CO)₅X have been performed. The emission quantum efficiency, but not the spectral distribution, is very sensitive to temperature, as evidenced by the large changes in emission intensity as the temperature is varied. (Figure 5). The emission quantum efficiency was determined at the lowest temperature accessible with the equipment available using a technique recently reported.²⁵ The quantum efficiency at another temperature was assumed to be the ratio of the emission area at the temperature to the emission area at the lowest temperature times the quantum efficiency at the lowest temperature. A possible major error here is the difference in percent light absorbed by the solid at the various temperatures, but we have found that these changes are small in the temperature range of interest: 25–100 K. The quantum efficiencies and temperature dependencies were determined several times and the data are summarized by the plots shown in Figure 6. The emission lifetimes were also determined as a function of temperature and the results are included in Figure 6. For each Re(CO)₅X complex over the entire temperature range studied we find that $\Phi(T_1)/\Phi(T_2)$ equals $\tau(T_1)/\tau(T_2)$ where $\Phi(T_1)$ and $\Phi(T_2)$ are the emission quantum efficiencies at temperatures T_1 and T_2 , respectively, and $\tau(T_1)$ and $\tau(T_2)$ are the emission lifetimes at the same two temperatures. Luminescence data are summarized in Table III.

c. **Photochemistry.** The photochemistry of Re(CO)₅X has been studied at 25 °C in degassed CCl₄ solution. The disappearance quantum yields of Re(CO)₅X were determined by measuring the decline in the absorbance at a

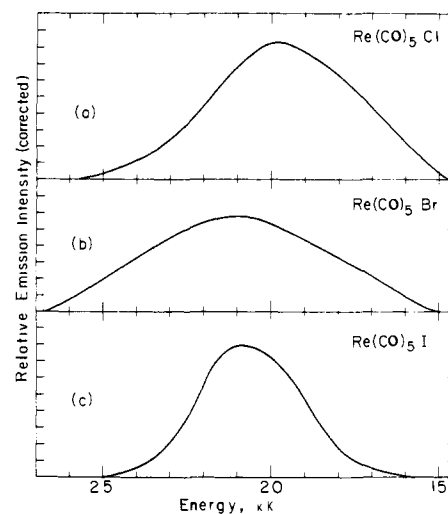


Figure 4. Corrected emission spectra at 25 K of pure powdered Re(CO)₅X. Excitation wavelength is 370 nm.

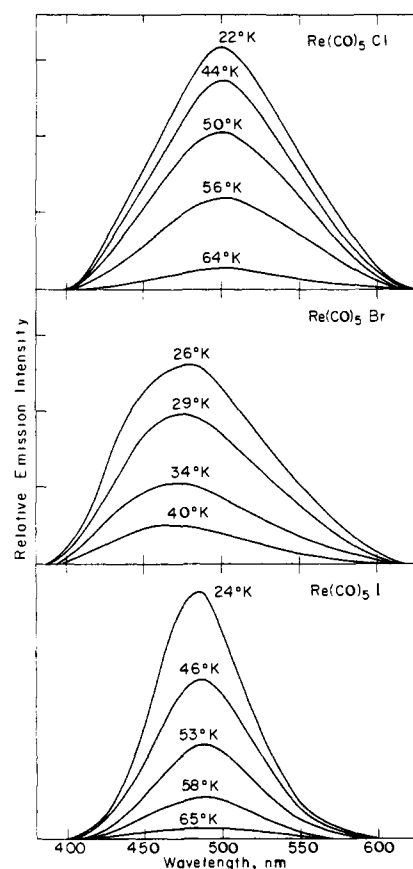


Figure 5. Traced emission spectra of pure powdered Re(CO)₅X as a function of temperature. Excitation wavelength is 370 nm.

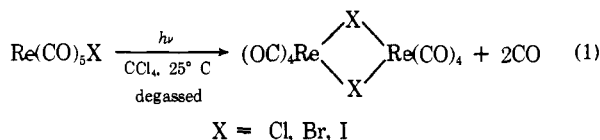
near-ir overtone absorption. The bands monitored and their molar absorptivities are as follows: X = Cl, 4193 cm⁻¹ (ϵ 9.6); X = Br, 4189 cm⁻¹ (ϵ 19.5); and X = I, 4181 cm⁻¹ (ϵ 21.6). Photolysis of Re(CO)₅X in CCl₄ proceeds according to reaction 1, and the products were identified by their characteristic ir absorptions²⁷ in the CO stretching region (Table IV). Since the [Re(CO)₄X]₂ species possibly form via dimerization of two photogenerated Re(CO)₄X coordinatively unsaturated intermediates, the quantum efficiency for formation of the product is not an accurate measure of the absolute efficiency for dissociative loss of CO from Re(CO)₅X. If dissociative loss of CO does occur, it is clear

Table III. Emission Data for $\text{Re}(\text{CO})_5\text{X}$ Complexes

X	Half-width of ^a band I, cm^{-1}	Emission ^b maximum, kK	Emission ^b half-width, cm^{-1}	Φ^b	$10^6\tau^b$
Cl	1500 ± 100	19.9 ± 0.2	5200 ± 200	$0.09 \pm 20\%$	$5.70 \pm 10\%$
Br	1440	21.0	6700	0.02 _s	2.21
I	1000	20.8	3630	0.33	14.0

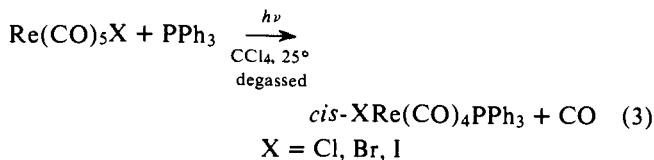
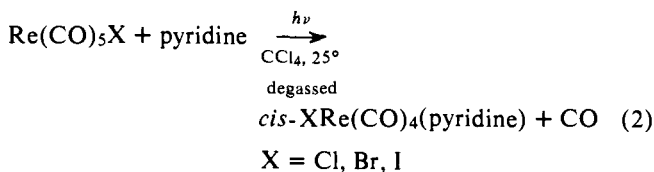
^a At 77 K in EPA solution. ^b At 26 K for pure solid $\text{Re}(\text{CO})_5\text{X}$. Values for emission maximum and half-width are taken from Figure 3 and values for Φ and τ are from Figure 5. Excitation λ 370 nm for Φ .

that the CO concentration at least equals the $\text{Re}(\text{CO})_4\text{X}$ concentration and capture of CO to regenerate $\text{Re}(\text{CO})_5\text{X}$ may compete with reaction 1. However, high chemical yields (initially quantitative) for $[\text{Re}(\text{CO})_4\text{X}]_2$ serve to show that CO substitution is an important photoreaction. Disappearance yields for $\text{Re}(\text{CO})_5\text{X}$ under the conditions indicated in reaction 1 are given in Table V for 313 and 366



nm photolysis at 6.65×10^{-8} and 1.0×10^{-7} einstein/min, respectively. The quantum efficiency at 366 nm is markedly lower than at 313 nm, even though the light intensity at 366 nm is slightly larger than at 313 nm. The higher intensity could result in a higher observed quantum yield since a higher steady-state concentration of $\text{Re}(\text{CO})_4\text{X}$ intermediates should result.

Irradiations of $\text{Re}(\text{CO})_5\text{X}$ in the presence of pyridine and PPh_3 proceed according to reactions 2 and 3, respectively. Ir band maxima for the known compounds²⁸ are included in Table IV. Though *trans*- $\text{BrRe}(\text{CO})_4\text{PPh}_3$ is a known compound,²⁹ we find no evidence for its formation here. In fact, we have carefully examined the ir spectra of the photoproducts as compared to the thermal products²⁸ obtained from reaction of PPh_3 with $[\text{Re}(\text{CO})_4\text{X}]_2$ and have found them to be the same. Disappearance quantum yields for $\text{Re}(\text{CO})_5\text{X}$ at 366 and 313 nm under conditions of reactions 2 and 3 are given in Table V.



The disappearance yields for these two reactions are the same within experimental error at 366 nm, and for reaction 2 the 313 nm yield is higher than the 366 nm yield found for reaction 1. Strong absorption at 313 nm by PPh_3 precludes a quantum yield measurement at this wavelength for reaction 3.

Several other aspects of the photochemistry of $\text{Re}(\text{CO})_5\text{X}$ are worth noting. First, photolysis of $\text{Re}(\text{CO})_5\text{X}$ in solutions containing 1,10-phenanthroline leads to quantitative yields of $\text{XRe}(\text{CO})_3(1,10\text{-phenanthroline})$. Likewise photolysis of $\text{Re}(\text{CO})_5\text{X}$ in the presence of other donors, including EtOH, CH_3CN , 4-styrylpyridine, etc., produces spectral changes consistent with CO substitution. In none of the cases which we have investigated quantitatively (reac-

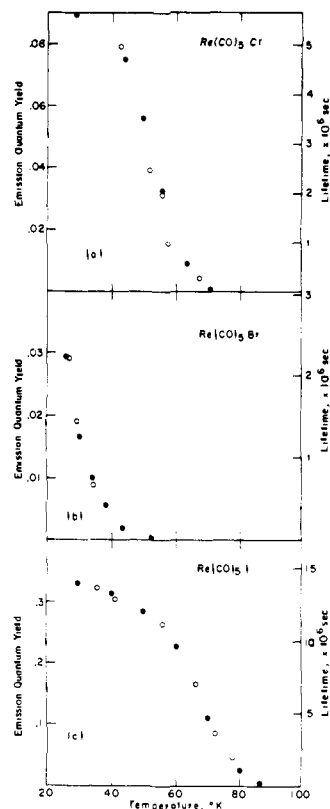


Figure 6. Temperature dependence of emission lifetimes (●) and quantum yields (O) for pure powdered $\text{Re}(\text{CO})_5\text{X}$. Excitation wavelength is 370 nm.

tions 1-3) nor in the qualitative cases just mentioned do thermal CO substitution rates at 25 °C compete with the photosubstitution. Finally, with regard to qualitative aspects of the photochemistry we have been unable to detect either the generation of intermediates or net chemical changes upon photolysis of $\text{Re}(\text{CO})_5\text{X}$ at 77 K in EPA or EtOH solution. While it is exceedingly difficult to make measurements of quantum yields at 77 K, we estimate the yields to be no less than 50 times smaller than at 300 K, nor do we find evidence for extreme photosensitivity of the solids at room temperature. At 200 K in solution, though, we do find that the complexes are photosensitive. As an example the spectral changes upon photolysis of $\text{Re}(\text{CO})_5\text{I}$ at 200 K in EtOH are irreversible and are comparable to those occurring at 300 K in the same photolysis time.

Discussion

Band I is associated with the $^1A_1(e^4b_2^2) \rightarrow ^3E(e^3b_2^2a_1^1)$ spin-forbidden transition in $\text{W}(\text{CO})_5(\text{amine})$,¹¹⁻¹³ and we adopt this assignment here for band I in all the C_{4v} Re complexes and for $[\text{W}(\text{CO})_5\text{Br}]^-$. Band I is absent or unobservably weak in the Cr, Mo, and Mn complexes studied. This fact is consistent with the spin-forbidden nature of the transition, which is overcome by the large degree of spin-orbit coupling associated with the heavy, third-row Re and W

Table IV. Ir Maxima (cm⁻¹) in CO Stretching Region for Rhenium Complexes

Compound	This work in isoctane			Literature in CCl ₄ ^a				
Re(CO) ₅ Cl	—	2045 (s)	—	1980 (m)	2156 (w)	2045 (s)	2016 (w)	1982 (m)
Re(CO) ₅ Br	—	2043 (s)	—	1980 (m)	2150 (w)	2045 (s)	2016 (w)	1984 (m)
Re(CO) ₅ I	2142 (w)	2042 (s)	2010 (w)	1985 (m)	2145 (w)	2042 (s)	2013 (w)	1987 (m)
[Re(CO) ₄ Cl] ₂	2110 (w)	2029 (s)	2000 (m)	1962 (m)	2114 (w)	2032 (s)	2000 (m)	1959 (m)
[Re(CO) ₄ Br] ₂	2110 (w)	2030 (s)	1998 (m)	1960 (m)	2113 (w)	2031 (s)	2000 (m)	1964 (m)
[Re(CO) ₄ I] ₂	2103 (w)	2025 (s)	1998 (m)	1960 (m)	2106 (w)	2029 (s)	2001 (m)	1965 (m)
cis-ClRe(CO) ₄ (py)	—	2005 (s)	1940 (s)	—	2111 (m)	2009 (vs)	1934 (s)	—
cis-BrRe(CO) ₄ (py)	—	2005 (s)	1930 (s)	—	2110 (m)	2008 (vs)	1936 (s)	—
cis-IRe(CO) ₄ (py)	—	1998 (s)	1930 (s)	—	2105 (m)	2005 (vs)	1938 (s)	—
cis-ClRe(CO) ₄ PPh ₃	—	2020 (s)	1995 (s)	1945 (s)	2106 (m)	2018 (s)	2002 (vs)	1945 (s)
cis-BrRe(CO) ₄ PPh ₃	2105 (m)	2020 (s)	2002 (s)	1945 (s)	2107 (m)	2020 (s)	2003 (vs)	1947 (s)
cis-IRe(CO) ₄ PPh ₃	2100 (m)	2020 (s)	2000 (s)	1945 (s)	2101 (m)	2018 (s)	2001 (vs)	1948 (s)

^a These data are found in ref 27, 28.

Table V. Reaction Quantum Yields for Re(CO)₅X^a

X	Reaction ^b no.	Φ _{366nm} ^c (±10%)	Φ _{313nm} ^d (±10%)
Cl	1	0.06	0.44
Br	1	0.18	0.65
I	1	0.08	0.35
Cl	2	0.20	0.76
Br	2	0.34	0.58
I	2	0.10	0.67
Cl	3	0.21	—
Br	3	0.31	—
I	3	0.07	—

^a Reactions carried out in CCl₄ and measured by monitoring decline of near-ir CO overtone of Re(CO)₅X. ^b Reaction number 1 corresponds to formation of [Re(CO)₄X]₂; number 2 to XRe(CO)₄(py), and number 3 to formation of XRe(CO)₄PPh₃. ^c 1.0 × 10⁻⁷ einstein/min. ^d 6.65 × 10⁻⁸ einstein/min.

complexes. The corresponding spin-allowed ¹A₁(e⁴b₂²) → ¹E(e³b₂²a₁¹) transition is associated with band II in W(CO)₅(amine),¹¹⁻¹³ and it is observed in the Cr and Mo analogues as expected. The Re and Mn species both exhibit band II. The relationship of bands I and II and the first transition (¹A_{1g} → ³T_{1g}) in the O_h metal hexacarbonyls is also as expected for the LF assignments: the first band occurs up to ~8000 cm⁻¹ lower in energy in the C_{4v} complexes. This large shift is as expected by comparison with the analogous transitions^{4,6} in M(CN)₆³⁻ and M(CN)₅X³⁻ (M = Co(III), Rh(III), Ir(III)); furthermore, the shift in band position is in reasonable qualitative agreement with a prediction based on the known LF strengths of CO and X. Finally, along these lines the lowest two absorption bands in Ir(CO)₅X³⁻, ¹A₁ → ^{1,3}E, are very similar to bands I and II reported here in shape and relative intensity,⁶ while only the ¹A₁ → ¹E absorption is observable⁶ in Rh(CN)₅X³⁻. In summary, the lowest energy absorption bands in the C_{4v} Re carbonyls conform nicely to the LF interpretation. In particular, substantial σ-X, π-X → Re, or σ-X, π-X → π*CO CT contributions to the lowest absorptions are ruled out by the spectral similarity of the halide complexes to W(CO)₅(amine). Even more convincingly, the spectral similarity of the [M(CO)₅NH₂CH₃]⁺ and the M(CO)₅(halide) demands a common assignment.

With the new electronic spectral data here we are now in a position to reassess some previous assignments of the electronic spectra of d⁶ metal carbonyls. First, the assignments for Mn(CO)₅X which have been either d_{xy}(b₂) → π*CO^{23c} or π-X(e) → π*CO²² are untenable. The data from the literature clearly show that the lowest band system in these complexes is analogous to band II, ¹A₁(e⁴b₂²) → ¹E(e³b₂²a₁¹), in Re(CO)₅X and W(CO)₅Y as well as in other low-spin d⁶, C_{4v} complexes.^{1-4,6} The corresponding spin-forbidden transition does not give rise to an observable

absorption, which is consistent with the relatively small degree of spin-orbit coupling in Mn compared to Re. Along these same lines, the spin-orbit coupling factor likely comes into play in decay phenomena in that Re(CO)₅Cl and W(CO)₅(amine) emit, whereas Cr(CO)₅X and Mn(CO)₅Cl do not.¹¹ The energetic dependence of the first band in Mn(CO)₅X with respect to X is as found in Re(CO)₅X and the M(CN)₅X³⁻ species.^{4,6} Further, the position of band II for a given X decreases according to Re(I) > Mn(I) > Cr(0), which is consistent with a LF assignment.

One point concerning [Mn(CO)₆][BF₄] is worth noting at this time. The lowest absorption band at 33 250 cm⁻¹ (ε 600 l. mol⁻¹ cm⁻¹) is seemingly too intense to be ascribed to the spin-forbidden ¹A_{1g}(t_{2g}⁶) → ³T_{1g}(t_{2g}⁵e_g¹) transition. This comment is provoked by the absence of any observable singlet to triplet absorptions in any of the other first-row low-spin d⁶ systems of either O_h or C_{4v} symmetry. We, therefore, reassign this band to the corresponding spin-allowed transition, ¹A_{1g} → ¹T_{1g}. The bands which appear at 37 300 and 39 600 cm⁻¹ may well be vibrational components of the ¹A_{1g}(t_{2g}⁶) → ¹T_{2g}(t_{2g}⁵e_g¹) transition or weak, low energy M → π*CO CT excitation.

A LF interpretation in Cr(CO)₅X is appropriate, but assignment^{16a} of the lowest absorption as ¹A₁(e⁴b₂²) → ¹E(e³b₂²b₁¹) is unlikely for two reasons. First, population of d_{x²-y²}(b₁) is inconsistent with the photochemistry observed upon irradiation into the lowest absorption band of M(CO)₅(amine) complexes, where the M-amine bond is labilized (z axis labilization).¹¹⁻¹³ Second, even if the one-electron energy of b₁ is lower than that of a₁, the lowest transition would still likely be predominantly e → a₁, as destabilization owing to interelectronic repulsion is much more pronounced in ¹E(e³b₂²b₁¹) than in ¹E(e³b₂²a₁¹).³⁰ Thus, in view of these arguments, the ¹A₁(e⁴b₂²) → ¹E(e³b₂²a₁¹) assignment best accounts for all of the known pertinent facts.

Our conclusions are in essential agreement with those of McLean,¹⁵ but for Re(CO)₅X we adopt the ¹A₁(e⁴b₂²) → ³E(e³b₂²a₁¹) assignment for the first absorption band without equivocation based on the emission results and the lack of a similar band in the first-row analogues. The fact that PES data^{20,21} for the M(CO)₅X (M = Mn, Re; X = Cl, Br, I) show that the highest occupied orbital is mainly halogen in character does cause confusion here, but it must be emphasized that one-electron orderings do not always lead to correct predictions of the relative positioning of electronic transitions.³¹ The notion that we are simply arguing about how much π-X character is in the lowest e → d_{2z}(a₁) transition is inconsistent with the strong similarity in the spectra of M(CO)₅(halide) and M(CO)₅(amine) for all M investigated. Electronic absorption spectral data in Table I are best accommodated by assigning bands I and II to the

${}^1A_1(e^4b_2^2) \rightarrow {}^3E(e^3b_2^2a_1^1)$ transitions with the understanding that the π -X and d_{xz} , d_{yz} orbitals do mix by symmetry. Thus, for the pentacarbonylhalogeno complexes, the lowest absorption must have some π -X \rightarrow M CT character, but in every case listed in Table I the lowest transition is mainly LF and more so for group 6 than for group 7 complexes.¹⁵

We now consider briefly bands III and IV, which appear in $\text{Re}(\text{CO})_5\text{X}$ and seem to have counterparts in the $\text{W}(\text{CO})_5\text{Y}$ complexes. One difference is that band III in $\text{W}(\text{CO})_5\text{Y}$ is split into at least two components, whereas it is not split in $\text{Re}(\text{CO})_5\text{X}$. Band IV appears in $\text{Re}(\text{CO})_5\text{X}$ and $\text{W}(\text{CO})_5\text{Y}$ and has similar shape, relative position, and intensity in both systems. The weaker band III may be associated with either the orbitally forbidden ${}^1A_1(e^4b_2^2) \rightarrow {}^1A_2(e^4b_2^1b_1^1)$ or the spin-forbidden ${}^1A_1(e^4b_2^2) \rightarrow {}^3E(e^3b_2^2b_1^1)$ transition. In any case, population of the $d_{x^2-y^2}(b_1)$ orbital occurs in these higher energy transitions.

The very high energy, high intensity band V, which has several components, is associated with metal $\rightarrow\pi^*(\text{CO})$ CT. Curiously, in no portion of the high energy region of the spectra of $\text{M}(\text{CO})_5(\text{amine})$ and $\text{M}(\text{CO})_5(\text{halide})$ do we find evidence of any major differences. This fact is in reasonable agreement with expectation,⁴ as the σ -X $\rightarrow d_{z^2}(a_1)$ transition should be at very high energy, and π -X $\rightarrow d_{z^2}(a_1)$ should have fairly low intensity.

The emission band is logically associated with the lowest absorption system and is assigned to the ${}^3E(e^3b_2^2a_1^1) \rightarrow {}^1A_1(e^4b_2^2)$ transition. Though there is some overlap of emission and absorption, the emission band is very broad and suggests a large geometrical distortion in ${}^3E(e^3b_2^2a_1^1)$ as compared to the ${}^1A_1(e^4b_2^2)$ ground state. This distortion is likely an elongation of the X-Re-CO axis due to the σ -antibonding nature of the $d_{z^2}(a_1)$ orbital. Such a distortion substantially reduces the LF strength along the z axis, thereby lowering the energy of the ${}^3E(e^3b_2^2a_1^1)$ state. This situation contrasts with that observed for $\text{W}(\text{CO})_5(\text{amine})$, where the emission is not as red-shifted from the ${}^1A_1 \rightarrow {}^3E$ absorption, nor is the emission from $\text{W}(\text{CO})_5(\text{amine})$ as broad as the emission from $\text{Re}(\text{CO})_5\text{X}$. These differences may be due to the fact that the distortion in $\text{Re}(\text{CO})_5\text{X}$ involves substantial weakening of the axial Re-C bond, whereas for $\text{W}(\text{CO})_5\text{NH}_3$ the distortion likely involves the W-N bond. The contrast in distortions is important because even total dissociation of the amine to generate $\text{W}(\text{CO})_5$ should not yield a large change in excited-state energies, as the lowest absorption band maximum at $22\,727\text{ cm}^{-1}$ ($\epsilon\ 6300\text{ l. mol}^{-1}\text{ cm}^{-1}$) for $\text{W}(\text{CO})_5^{13}$ is fairly close to that for $\text{W}(\text{CO})_5(\text{amine})$. For $\text{Re}(\text{CO})_5\text{X}$, though, the tendency is to lose CO, which would likely have a large effect on the position of the lowest excited state.

The strongly temperature dependent emission found here is the first quantitative data of this type for metal carbonyls. In other low-spin d^6 systems, where both CT and LF assignments are made, the temperature dependent emissions are rationalized by assuming that a set of spin-orbit states of differing decay properties which lie close together are thermally equilibrated.³² For the case at hand, the ${}^3E(e^3b_2^2a_1^1)$ state splits into E, A_1 , A_2 , B_1 , and B_2 components upon inclusion of spin-orbit coupling. The $A_1 \rightarrow A_1$, E components are orbitally allowed. Thus, assuming the spin-orbit model, A_1 and E are likely the lowest lying states, as the radiative efficiency increases monotonically down to 25 K. However, the fact that

$$\Phi(T_1)/\Phi(T_2) = \tau(T_1)/\tau(T_2)$$

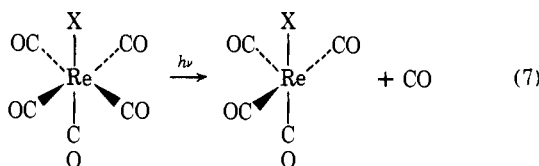
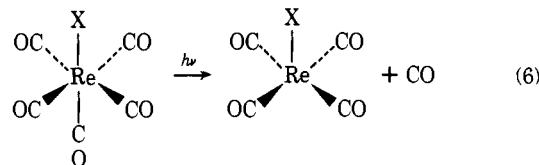
is only possible in a strict sense for a situation where the nonradiative constant, k_{nr} , and not the radiative constant,

k_r , changes with variation in temperature. This requirement follows from the definition of emission lifetime, τ , eq 4, and the emission quantum yield, Φ , eq 5. An invariant k_r , even though the population of the spin-orbit states changes with temperature, is unexpected.

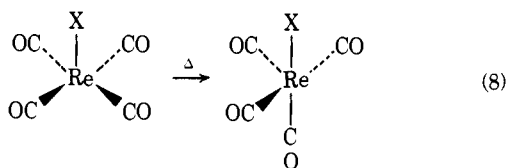
$$\tau = \frac{1}{k_{nr} + k_r} \quad (4)$$

$$\Phi = \frac{k_r}{k_{nr} + k_r} \quad (5)$$

Finally, we consider the photosubstitution behavior of the $\text{Re}(\text{CO})_5\text{X}$ species. The chemical products reflect the fact that CO substitution is the important primary photoprocess. A dissociative mechanism of CO substitution is supported by the similar quantum yields for PPh_3 and pyridine substitution at 366 nm and the fact that the $[\text{Re}(\text{CO})_4\text{X}]_2$ dimers form efficiently in the absence of nucleophiles. Two stereochemical possibilities exist, reaction 6 and reaction 7, fea-



turing loss of the CO on the z axis or one of the CO's on the x and y axes. At this time the important observation is that we see smaller CO substitution yields upon 366 than 313 nm photolysis. These two wavelengths correspond to the population of the $d_{z^2}(a_1)$ and $d_{x^2-y^2}(b_1)$ orbitals, respectively, and we ascribe the variation in quantum yields with wavelength to this difference. By analogy, an increase in CO substitution efficiency of $\text{W}(\text{CO})_5(\text{amine})$ was found¹¹⁻¹³ upon population of $d_{x^2-y^2}(b_1)$ and similarly an increase in CN⁻ substitution was found^{6b} for $\text{Co}(\text{CN})_5\text{OH}_2^{2-}$ and $\text{Co}(\text{CN})_5\text{OH}^{3-}$ upon irradiation in a region corresponding to population of this orbital. The relative lack of halide substitution is consistent with the models^{9,10} proposed for substitutional reactivity of LF excited states, as the halides are π -donor ligands and can more fully exploit π -bonding possibilities when the d_{xz} , $d_{yz}(e)$ orbitals are depopulated in the lowest LF state. This situation is in contrast to that for $\text{W}(\text{CO})_5(\text{amine})$ where W-N cleavage is the main result¹³ of population of the $d_{z^2}(a_1)$ orbital. The lability of the amine relative to the halide is rationalized by the fact that the amine is only a σ -donor ligand and no strengthening of π -bonding is possible by depopulation of the $d_{xz}, d_{yz}(e)$ orbitals. We propose that reaction 6 is a consequence of population of the $d_{z^2}(a_1)$ orbital and that reaction 7 is associated with the population of the $d_{x^2-y^2}(b_1)$ orbital. The unusually high CO substitution yield for the upper excited state reaction (eq 7) may be related to the fact that the CO's cis to X are also probably the most labile in the ground state.³³ The conclusion that axial CO is labilized (reaction 6) by population of the $d_{z^2}(a_1)$ orbital upon 366 nm photolysis is seemingly inconsistent with the absence of *trans*- $\text{Re}(\text{CO})_4\text{XPPH}_3$ products, which are likely to be stable at 300 K. We can rationalize the absence of these products, though, by invoking the irreversible rearrangement indicated in reaction 8, followed by capture of the nu-



cleophile to yield *cis*- $\text{Re}(\text{CO})_4\text{XL}$ products. A less satisfying alternative is that even at 366 nm there is enough labilization of the equatorial CO's to overcome the lability of the axial CO. The formation of *cis*- $\text{Re}(\text{CO})_4\text{XL}$ at 313 nm is consistent with population of $d_{x^2-y^2}(b_1)$. A definitive assessment of the stereochemistry of the photosubstitution must, however, await the results of photoinduced ^{13}C exchange.

In the quantum yields for reactions 1–3 we point out a clear trend: for the 366-nm photolysis the order of reactivity is $\text{Re}(\text{CO})_5\text{Br} > \text{Re}(\text{CO})_5\text{Cl} > \text{Re}(\text{CO})_5\text{I}$. The ordering correlates in a reasonable way with certain aspects of the luminescence phenomena, where we find that (1) the emission bandwidths seem to be ordered $\text{Re}(\text{CO})_5\text{Br} > \text{Re}(\text{CO})_5\text{Cl} > \text{Re}(\text{CO})_5\text{I}$ and (2) $\text{Re}(\text{CO})_5\text{I}$ emits at the highest temperature, $\text{Re}(\text{CO})_5\text{Cl}$ is intermediate, and the lowest temperatures are needed to produce luminescence in $\text{Re}(\text{CO})_5\text{Br}$. A final point relating to photochemical reactivity concerns the lack of efficient CO dissociation at ≤ 77 K in solution. This fact is probably due both to the incomplete eradication of the Re–CO interaction and the relatively rigid medium. This result provokes some questions as to the difference in this CO photodissociation and the several systems¹³ where this reaction is easily observed in matrix and glassy media at low temperatures (77 K). Measurement of the quantum yields of CO dissociation at low temperature is now in progress.

Experimental Section

Materials. All of the complexes investigated here are well-characterized, well-known compounds. $\text{Re}(\text{CO})_5\text{Cl}$ and $\text{Re}(\text{CO})_5\text{Br}$ were obtained from Pressure Chemical Co. and purified by sublimation. The $\text{Re}(\text{CO})_5\text{I}$, $\text{W}(\text{CO})_5\text{NH}_3$, $[(\text{C}_2\text{H}_5)_4\text{N}][\text{W}(\text{CO})_5\text{Br}]$, $[(\text{C}_2\text{H}_5)_4\text{N}][\text{Cr}(\text{CO})_5\text{Br}]$, and the $[\text{M}(\text{CO})_5\text{NH}_2\text{CH}_3]\text{Cl}$ were prepared and purified according to procedures outlined in the literature.^{26,34} All solvents used are commercially available and were checked for spectral purity in the wavelength ranges of interest.

Absorption Spectra. All ir spectra used to identify photoproducts were measured on a Perkin-Elmer 337 or 521 ir spectrometer using either matched 0.1 or 1.0 mm path length NaCl cells. The CO stretching overtone spectra of $\text{Re}(\text{CO})_5\text{X}$ and all electronic absorption spectra were measured using a Cary 17 uv-vis-nir absorption spectrophotometer. Room temperature spectra were generally measured in 1.0-cm path length cuvettes, but spectral changes accompanying photolyses were monitored using the 13×100 mm test tube reaction vessel in a round cell holder for the Cary 17. Absorption spectra at 77 K were measured using either EPA or EtOH as the solvent. The 77 K spectra were run using an all-quartz liquid N_2 Dewar equipped with optical quality quartz flats for windows. The round, ~ 1 -cm path length, quartz cell containing the sample remained in contact with liquid N_2 during the absorption measurement. Some 77 K spectra and all spectra below 77 K were measured using a Cryogenic Technology, Inc. Spectrim II sample conditioner. The samples were dissolved in EPA or EtOH and put in a round quartz tube approximately 2 cm long and 0.3 cm in diameter. The tube was tightly stoppered with a cork and wedged into an all-copper cell holder in direct thermal contact with the cold-tip of the Spectrim II. The corked sample did not leak when subjected to the vacuum of the Spectrim II sample chamber. The external quartz shroud surrounding the copper cell holder was masked with black electrical tape to ensure that only the sample was in the light beam of the Cary 17. Generally, the sample did not remain glassy below 77 K, but the crystallization of the sample was not so extensive as to preclude spectral measurements. In the spectra shown in Figure 1 we have not corrected the spectral changes upon cooling for solvent contraction. The spectrum of $\text{Re}(\text{CO})_5\text{Cl}$ as a thin film

was recorded using the Cary 17. The thin film was prepared by evaporating a CH_2Cl_2 solution of $\text{Re}(\text{CO})_5\text{Cl}$ on a quartz flat.

Emission Spectra. For the emission studies an Aminco-Bowman emission spectrophotometer was set up for measurements in the 200–900-nm range and equipped with a grating blazed at 750 nm. The PMT detector used was a Hamamatsu R136 operated at 750 V and 25 °C. Both emission and excitation monochromators were calibrated using a low pressure Hg lamp. The relative sensitivity of the detection system was calibrated over the entire 300–900 nm range by a standard lamp obtained from and calibrated by E. G. & G. Inc., Salem, Mass. The standard lamp is a 200-W tungsten halogen lamp operated at 6.50 A having serial number B115A and was calibrated from NBS QM 197, QM 198, QM 199. Thus, the emission spectra in Figure 4 are corrected spectra.

Emission quantum yields for pure, powdered $\text{Re}(\text{CO})_5\text{X}$ were measured according to a published procedure,²⁵ and temperature variation was achieved using the Spectrim II. Emission lifetimes were measured using the instrumentation previously described³⁵ and plots of log (emission intensity) against time were linear over at least two lifetimes. Lifetimes and quantum yields in Figure 6 and Table III are the result of at least triplicate determinations. The lack of vibrational-structure on the emission does not seem to be limited by the resolution of the Aminco, as we could easily observe the richly vibrationally structured emission of ruthenocene^{25b} under the same conditions.

Photochemistry of $\text{Re}(\text{CO})_5\text{X}$. Three-milliliter aliquots of CCl_4 solutions of $\text{Re}(\text{CO})_5\text{X}$ with or without added pyridine (0.1 M) or PPh_3 (0.1 M) were placed in 13×100 mm test tubes with constrictions. The samples were freeze-pump-thaw degassed in at least three cycles and hermetically sealed. Photolyses of the samples were carried out in merry-go-rounds equipped with 450-W or 550-W Hanovia medium pressure Hg lamps filtered to isolate either the 313 or 366 nm emission. The light intensities were measured using ferrioxlate actinometry.³⁶ The disappearance quantum yields of $\text{Re}(\text{CO})_5\text{X}$ were measured for small conversions ($< 15\%$) by monitoring the decline of a near-ir CO stretching overtone of $\text{Re}(\text{CO})_5\text{X}$ using the 0.1 slidewire of the Cary 17. No interferences were encountered at the near-ir absorption bands that were monitored. No particular difficulty exists when monitoring the concentration of a substance by this spectrophotometric technique. Typically, however, near-ir absorptions are very weak and solvent absorptions mask bands due to the solute. In the present case we were able to take advantage of the facts that the metal carbonyls have relatively intense near-ir overtone absorptions and that the solvent could be CCl_4 which is transparent in the near-ir. The use of near-ir overtones to monitor reactions like those described herein is a good technique because the bands are well resolved and quite characteristic of the particular metal carbonyl. Identification of the products, though, was carried out by ir spectral measurements in the CO stretching region of irradiated iso-octane solutions of $\text{Re}(\text{CO})_5\text{X}$. Alkane solutions yield the sharpest, most well-resolved ir spectra of the metal carbonyls. The product identification was also carried out in CCl_4 solutions to ensure that the quantum yields actually measured correspond to the formation of the substitution product and not a reaction product of the CCl_4 . In all cases, prolonged irradiation leads to other photoproducts as yet uncharacterized, which result in colored (other than yellow) solutions in either CCl_4 or iso-octane. The primary photoreaction of $\text{Re}(\text{CO})_5\text{X}$ is only CO release, since we initially find quantitative chemical yields for $[\text{Re}(\text{CO})_4\text{X}]_2$ in iso-octane.

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Substituent Effects in Cluster Species. Photoelectron Spectra of 1-, 2-, and μ -Substituted Pentaborane(9)

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Abstract: The He(I) photoelectron spectra of 1- and 2-XB₅H₈ where X = Cl, Br, I, and CH₃ and 1-, 2-, and μ -SiH₃B₅H₈ are reported. The effect of substitution on one of the skeletal molecular orbitals of the borane fragment is examined and analyzed using a LCBO model. It is shown that the relative isomer stabilities may be understood in terms of two effects: the relative potential at the substituent atom due to the position of substitution on the borane framework (an example of Bent's rule) and the relative strength of conjugative interactions at the different positions of substitution. The analysis is also consistent with the measured relative acidities of the compounds.

Many elements possess an affinity for multicenter bonding which exhibits itself in the formation of cluster species.¹ The boranes and carboranes constitute one system in which there is great variety in cluster formation.² It is also a system which has been extensively studied both theoretically and experimentally and, as a result, the principle of the separation of a skeletal bonding system from the exo-skeletal bonding system has been established.³⁻⁵ This has led to a correlation between the geometrical structure of the cluster and the number of skeletal electrons.⁶⁻⁸ As the number of electron pairs increases in an *n* atom cluster from *n* + 1 to *n* + 2 to *n* + 3, the cluster structure changes from a closo (triangular faced polyhedron with *n* vertices) to nido (polyhedron with *n* + 1 vertices, one of which is vacant) to arachno (polyhedron with *n* + 2 vertices, two of which are vacant). It has been pointed out that similar considerations apply to metal carbonyl clusters and transition metal π -complexes and, thus, may be important in understanding cluster formation in general.^{7,9}

Clearly, any exo-endo separation is not rigorous and exo

atoms or groups must affect the skeletal bonding by the usual electron donating and withdrawing mechanisms. Although these effects may not be evident in the gross structure, they would certainly affect chemical reactivity, for example. The investigation of substituent effects should result in a deeper understanding of cluster species. As boranes serve as structural prototypes of cluster species^{7,9,10} they should also serve as models for investigating cluster substituent effects. This aspect of borane chemistry has not been neglected, having been examined from both the theoretical¹¹ and experimental points of view.¹²⁻¹⁴ However, important questions, such as explaining observed relative isomer stabilities, are only beginning to be answered.

A relatively recent technique, photoelectron spectroscopy, yields direct information on the electronic structure of ions and yields a representation of the molecular orbital structure of molecules.¹⁵ As such it is ideally suited to investigate the effects of substituents on electronic structure and it has been fruitfully used for this purpose on a number of previous occasions.¹⁶ In the following we report the pho-