Chemical Reviews

Volume 74, Number 4 August 1974

The Photochemistry of Metal Carbonyls

MARK WRIGHTON

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received June 19, 1973 (Revised Manuscript Received October 9, 1973)

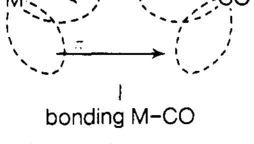
Contents

I. Introduction

Metal carbonyl complexes are among the most photoreactive transition metal complexes known, and the purpose of this article is to acquaint the reader with results related to the photochemistry of metal carbonyls and their derivatives. Reviews of metal carbonyls are numerous,[1] but only a few deal specifically with excited-state processes.[2-5] We review here all metal carbonyl photoprocesses including electronic absorption phenomena, luminescence, nonradiative decay, energy transfer, and chemical reaction. The use of light as a synthetic tool in this field became important in the late 1950's and early 1960's, and the last substantial review of the photochemistry appeared in 1969.[2] This paper centers on developments since that time, but emphasis is on a critical evaluation of all published material and enough data are presented to establish some generalities.

Metal carbonyls are known for numerous low-valent metals; four-, five-, six-, and seven-coordination are found; and formal d^n configurations include largely d^4, d^5, d^6, d^7, d^8, d^9, and d^{10}. Table I lists the elements whose carbonyl complexes have been the object of photochemical investigations (*vide infra*). At the present time, correlations between electronic structure and reactivity are in primitive stages of development so I have organized the material according to the central metal involved. The first section describes the work with group VI metal carbonyls since this group is the most well studied and can be used to illustrate several important concepts and generalities. The subsequent sections deal with the group V, group VII, and group VIII metal carbonyls in the order found in the periodic table.

It is widely believed that the bonding between CO and a metal is a combination of σ- and π-bonding.[6] Delocalization of π–d electrons from the central metal into the π^* CO orbital gives rise to π-back-bonding, and overlap of σ symmetry orbitals of the metal and CO yields a strong σ-donor interaction for the CO as diagrammed in I. The relative importance of σ and π interactions are difficult to assess, but one generally associates stronger π-back-bonding with lower valent metals which have a greater tendency to delocalize electron density into the ligand. Thus, we associate stable carbonyl complexes with low-valent metals. As a consequence of the large degree of delocalization of the electrons from the central metal into the ligand, these compounds are highly covalent. Therefore, electronic transitions involving these electrons should yield substantial changes in bonding, providing a general rationale for the extreme photosensitivity of the



I

bonding M–CO

TABLE I. Elements Known to Form Photoreactive Carbonyl Complexes

Group V	Group VI	Group VII	Group VIII		
V	Cr	Mn	Fe	Co	Ni
Nb	Mo	...	Ru	Rh	...
Ta	W	Re	Os	Ir	...

compounds. For d^n cases where n = 1–9, one expects the possibility of ligand field (LF) absorptions as well as charge-transfer (CT) transitions involving CO and the other ligands and the central metal. For some ligands one also must contend with the probability that intraligand excited states could be achieved.

The dominant photoreaction of $M(CO)_nL_x$ complexes is ligand substitution of either L or CO (eq 1 and 2).

$$M(CO)_nL_x \xrightarrow[Y]{h\nu} M(CO)_{n-1}YL_x + CO \quad (1)$$

$$M(CO)_nL_x \xrightarrow[Y]{h\nu} M(CO)_nL_{x-1}Y + L \quad (2)$$

While oxidative addition to photogenerated coordinatively unsaturated intermediates is common, there appears to be no definitive data that show that either photooxidation or photoreduction is a *primary* photoprocess upon uv or visible excitation. The photoassisted reaction of coordinated ligands is an area of importance, common reactions being either intramolecular rearrangements of L (eq 3) or

$$M(CO)_nL \xrightarrow{h\nu} M(CO)_nL' \quad (3)$$

addition with molecules in the medium (eq 4). One can also

$$M(CO)_nL \xrightarrow[h\nu]{L'} M(CO)_nL{-}L' \quad (4)$$

envision reactions involving the incorporation of CO into the ligand L. An emerging class of photoreactions of metal carbonyls is the fragmentation reactions of clusters as indicated in eq 5.

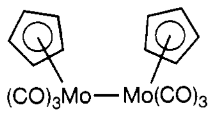
$$[M(CO)_x]_n \xrightarrow{h\nu} M(CO)_x + [M(CO)_x]_{n-1} \quad (5)$$

II. Chromium, Molybdenum, and Tungsten Carbonyls

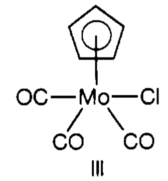
A. Geometrical Structure

The commonly known carbonyls of Cr(0), Mo(0), and W(0) are six-coordinate octahedral complexes, $M(CO)_6$.[7] Other stable complexes containing only the central metal and CO include the dimers $M_2(CO)_{10}^{2-}$ having a single M–M bond.[8] Numerous compounds of the $M(CO)_n(L)_{6-n}$ variety have been prepared, many photochemically.[2-5]

Complexes which are formally seven-coordinate are also found.[9] A typical example is the dimeric complex $Mo_2(CO)_6(\pi\text{-}C_5H_5)_2$ (II). Assuming $\pi\text{-}C_5H_5$ (Cp) to have a negative charge and to be a six-electron donor occupying three coordination sites, the central metal is in the +1 oxidation state. In complex III, though, it is appropriate to identify the central metal as being in a +2 oxidation state. Other complexes involving the +2 oxidation state are clearly seven-coordinate as exemplified by species such as $[W(CO)_2(diars)_2(I)]I$ and $Mo(CO)_3(L)I_2$ (L = bidentate ligand).[10] Finally, seven-coordinate compounds of the type $[W(CO)_3(diars)Br_2]^+$ can be obtained.[10] Thus, for the zerovalent metal complexes, six-coordination is common while for the +1, +2, and +3 oxidation states seven-coordination is found. Important work in the area of excited-state chemistry involves the six-coordinate compounds and π-cyclopentadienyl complexes like II and III.



II



III

B. Electronic Structure

Complexes of the general formula $M(CO)_n(L)_{6-n}$ have been given the most attention regarding electronic structure. The band position, intensity, and likely assignments for the electronic transitions for several types of Cr, Mo, and W carbonyls are set out in Table II.[11-27] Generally, the complexes exhibit a number of intense ($\epsilon > 10^2$) transitions in the uv-visible region which are associated with LF and M→L and L→M CT absorptions. Intraligand absorptions are indicated in several cases. The complexes of d^6 configuration are invariably diamagnetic.

Spectra for the $M(CO)_6$ (M = Cr, Mo, W) compounds were determined early,[28] and the lowest energy absorption at ~30,000 cm^{-1} was assigned as the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ LF absorption. The band appears only as a shoulder on the more intense M→π*CO CT absorption at ~35,0000 cm^{-1}. The second LF band, ${}^1A_{1g} \rightarrow {}^1T_{2g}$, predicted for d^6 O_h complexes, can be observed in the vicinity of ~37,500 cm^{-1} for the $M(CO)_6$ species. The most intense transition at ~43,000 cm^{-1} is assigned as a second component of the M→π*CO CT absorption. In later studies,[11] including the isoelectronic $V(CO)_6^-$, $Mn(CO)_6^+$ and $Re(CO)_6^+$ the same assignments were made except for one band at an energy below the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ absorption having ϵ ~1000 for $W(CO)_6$, ϵ 350 for $Mo(CO)_6$, and not present in the $Cr(CO)_6$. This low-energy absorption was identified as the lowest LF spin-forbidden singlet → triplet transition, ${}^1A_{1g} \rightarrow {}^3T_{1g}$. Spectra of $M(CO)_6$ in the low-energy region are shown in Figure 1. The enhanced intensity of the ${}^1A_{1g} \rightarrow {}^3T_{1g}$ transition with increasing atomic weight of the central metal is expected owing to the larger spin-orbital coupling in the heavier metal.[29] The constancy of the value of 10*Dq* of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ is due to a balancing of diminishing σ-bonding and increasing π-bonding for the heavier metal system.[11] While it has been argued[30] that *all* of the bands in these complexes are CT absorptions, the LF treatment provides the best rationale for the band positions including the lowest singlet → triplet absorption. Further, the LF approach accounts well for the observed spectral changes occurring upon substitution to yield $M(CO)_5(X)$ and $M(CO)_4(X)_2$ (*vide infra*). Finally, the intensities of the LF transitions are uncommonly large because of the high degree of covalency in these molecules; *i.e.*, the molecular orbitals have substantial contribution from both metal and ligand atomic orbitals tending to remove restrictions associated with the intensity of "d–d" transitions.

The one-electron energy level diagram for $M(CO)_6$ is shown in Scheme I. The ground electronic state, ${}^1A_{1g}$, has a t_{2g}^6 electronic configuration and the one-electron excitation to $t_{2g}^5e_g^1$ yields the ${}^{1,3}T_{1g}$ and ${}^{1,3}T_{2g}$ excited

SCHEME I

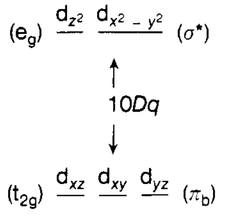


TABLE II. Electronic Transitions in Chromium, Molybdenum, and Tungsten Carbonyls

Complex	Bands, cm^{-1} (ϵ)	Assignment	Ref
$\mathrm{Cr(CO)_6}$[a]	29,500 (700) 31,550 (2670)	$^1A_{1g} \rightarrow {}^1T_{1g}$	11
	35,700 (13,100)	$^1A_{1g} \rightarrow c^1T_{1u}$	
	38,850 (3500)	$^1A_{1g} \rightarrow {}^1T_{2g}$	
	43,600 (85,100)	$^1A_{1g} \rightarrow d^1T_{1u}$	
$\mathrm{Mo(CO)_6}$[a]	28,850 (350)	$^1A_{1g} \rightarrow {}^3T_{1g}$	11
	30,150 (1690) 31,950 (2820)	$^1A_{1g} \rightarrow {}^1T_{1g}$	
	34,600 (16,800)	$^1A_{1g} \rightarrow c^1T_{1u}$	
	37,200 (7900)	$^1A_{1g} \rightarrow {}^1T_{2g}$	
	42,800 (138,000)	$^1A_{1g} \rightarrow d^1T_{1u}$	
$\mathrm{W(CO)_6}$[a]	28,300 (1000)	$^1A_{1g} \rightarrow {}^3T_{1g}$	11
	29,950 (1680) 31,850 (3250)	$^1A_{1g} \rightarrow {}^1T_{1g}$	
	34,650 (17,600)	$^1A_{1g} \rightarrow c^1T_{1u}$	
	37,100 (7400)	$^1A_{1g} \rightarrow {}^1T_{2g}$	
	43,750 (208,000)	$^1A_{1g} \rightarrow d^1T_{1u}$	
$\mathrm{Cr(CO)_5}$[b]	18,450 (3200)	$^1A_1 \rightarrow {}^1E$(?)	12
	42,194 (39,500)	M→π^*CO CT	
$\mathrm{Mo(CO)_5}$[b]	22,990 (3300)	$^1A_1 \rightarrow {}^1E$(?)	12
	40,820 (20,000)	M→π^*CO CT	
$\mathrm{W(CO)_5}$[b]	22,727 (6300)	$^1A_1 \rightarrow {}^1E$(?)	12
	42,194 (63,500)	M→π^*CO CT	
$\mathrm{Cr(CO)_5}$-(pyridine)[a]	25,640 (5600)	$^1A_1 \rightarrow {}^1E$(?)	13
	41,322 (34,700)	M→π^*CO CT	
$\mathrm{Cr(CO)_5PPh_3}$	27,855 (1400)	$^1A_1 \rightarrow {}^1E$(?)	14
$\mathrm{Cr(CO)_5}$-(piperidine)[d]	23,810 (3500)	$^1A_1 \rightarrow {}^1E$(?)	13
	40,000	M→π^*CO CT	
$\mathrm{Mo(CO)_5}$-($\mathrm{PPh_3}$)[d]	~29,200	$^1A_1 \rightarrow {}^1E$(?)	15
	~32,260	?	
	32,740 (3100)	?	
$\mathrm{Mo(CO)_5}$-(pyridine)[a]	25,975 (6600)	$^1A_1 \rightarrow {}^1E$	15
	41,150 (58,000)	M→π^*CO CT	
$\mathrm{Mo(CO)_5}$-(piperidine)[d]	25,130 (5000)	$^1A_1 \rightarrow {}^1E$	13, 15
	39,680 (58,000)	M→π^*CO CT	
$\mathrm{W(CO)_5}$-(pyridine)[d]	22,700 (630)	$^1A_1 \rightarrow {}^3E$	16, 17
	25,975 (6900)	$^1A_1 \rightarrow {}^1E$	
$\mathrm{W(CO)_5(ET_2NH)}$[d]	22,800 (730)	$^1A_1 \rightarrow {}^3E$	16, 17
	24,875	$^1A_1 \rightarrow {}^1E$	
$\mathrm{W(CO)_5}$-(cyclohexylamine)[d]	22,800 (520)	$^1A_1 \rightarrow {}^3E$	17
	24,875	$^1A_1 \rightarrow {}^1E$	
$\mathrm{W(CO)_5}$-(acetone)[d]	22,200 (910)	$^1A_1 \rightarrow {}^3E$	17
	24,630 (5100)	$^1A_1 \rightarrow {}^1E$	
$\mathrm{W(CO)_5(Et_2O)}$[d]	21,930	$^1A_1 \rightarrow {}^3E$	16
	23,920	$^1A_1 \rightarrow {}^1E$	
$\mathrm{W(CO)_5}$-(1-pentene)[d]	~25,975 (~550)	$^1A_1 \rightarrow {}^3E$	19
	27,780 (1530)	$^1A_1 \rightarrow {}^1E$	
	33,000 (7900)	?	
$\mathrm{W(CO)_5(PPh_3)}$[d]	27,500 (400)	$^1A_1 \rightarrow {}^3E$	18
	28,800 (2200)	$^1A_1 \rightarrow {}^1E$	
$\mathrm{W(CO)_5}$(*trans*-4-styrylpyridine)	~22,800 (5670)	$^1A_1 \rightarrow {}^3E$	20
	24,500 (7870)	$^1A_1 \rightarrow {}^1E$	
	31,650 (16,346)	Intraligand π–π^*	
$\mathrm{W(CO)_5}$(*trans*-2-styrylpyridine)	~22,800 (1230)	$^1A_1 \rightarrow {}^3E$	20
	25,130 (4800)	$^1A_1 \rightarrow {}^1E$	
	31,850 (17,900)	Intraligand π–π^*	
cis-$\mathrm{W(CO)_4}$(pyridine)$_2$[e]	21,600 (4740)	LF ($^1A_1 \rightarrow {}^3A_1, {}^3B_2$)	20
	24,200 (9370)	LF ($^1A_1 \rightarrow {}^1A_1, {}^1B_2$)	
	27,170 (7820)	(?)	
$\mathrm{Cr(CO)_4(phen)}$[e,g]			
In cyclohexane	16,950 (~5000)	M→π^* CT	21, 22
In $\mathrm{CH_3CN}$	21,370 (~5000)	M→π^* CT	
	37,370 (46,600)[c]	Intraligand $\pi \rightarrow \pi^*$	21, 22
$\mathrm{Mo(CO)_4(phen)}$[g]			
In cyclohexane	18,100 (~6300)	M→π^* CT	
In $\mathrm{CH_3CN}$	22,630 (~6300)	M→π^* CT	
	37,470 (52,500)[c]	Intraligand $\pi \rightarrow \pi^*$	21, 22
$\mathrm{W(CO)_4(phen)}$[g]			
In cyclohexane	17,640 (~8000)	M→π^* CT	
In $\mathrm{CH_3CN}$	21,980 (~8000)	M→π^* CT	
	37,380 (48,900)	Intraligand $\pi \rightarrow \pi^*$	
$\mathrm{Cr(CO)_3}$-(benzene)	~26,620	LF (?)	23, 25
	31,220	M→arene CT	
		M→π^* CO	
	~38,500	M→π^* CO	
$\mathrm{Cr(CO)_3}$-(aniline)[f]	~26,000	LF (?)	23, 25
	~31,000 (12,600)	M→arene, π^*CO	
	~38,500	M→π^* CO	
$\mathrm{Cr(CO)_5}$-$\mathrm{C(OC_2H_5)CH_3}$[d]	26,525 (5400)	(?)	27
	31,095 (6000)	(?)	
	41,102 (26,700)	M→π^*CO	
$\mathrm{W(CO)_5}$-$\mathrm{C(OC_2H_5)CH_3}$[d]	26,961 (7300)	(?)	27
	28,629 (7300)	(?)	
	35,162 (2000)	(?)	
	41,528 (56,700)	MM→π^*CO	
$\mathrm{Cr(CO)_4}$-(ethylenediamine)[c]	23,600 (1300)	LF ($^1A_1 \rightarrow {}^1A_1, {}^1B_2$)	21
	29,700 (5360)		
	35,500 (6300) 40,300 (18,200) 46,200 (21,900)	M→π^*CO CT + LF	
$\mathrm{Mo(CO)_4}$-(ethylenediamine)[c]	25,300 (1700)	LF ($^1A_1 \rightarrow {}^1A_1, {}^1B_2$)	21
	32,700 (10,000) 38,300 (20,000) 43,400 (20,000)	M→π^*CO CT + LF	
$\mathrm{W(CO)_4}$-(ethylenediamine)[c]	22,200 (400)	LF ($^1A_1 \rightarrow {}^3A_1, {}^3B_2$)	21
	25,200 (1400)	LF ($^1A_1 \rightarrow {}^1A_1, {}^1B_2$)	
	33,200 (8300) 39,200 (27,900) 45,000 (27,700)	M→π^*CO CT + LF	
$\mathrm{Cr(CO)_3}$-(mesitylene)[f]	~32,000 (12,600)	M→arene, π^*CO	24, 25
	38,500	M→π^*CO	
	45,450	M→π^*CO	
$\mathrm{Mo(CO)_3}$-(mesitylene)[f]	31,750 (8300)	M→arene, π^*CO	25
	34,700	M→π^*CO	
	39,500	M→π^*CO	
	43,500	M→π^*CO	
$\mathrm{W(CO)_3}$-(hexamethylbenzene)[c]	24,400 (563)	LF (?)	
	30,800 (15,000)	M→arene, π^*CO	26
	34,700 (6500)	M→π^*CO	
	42,000 (~1500)	. . .	
(benzene)-$\mathrm{Cr(CO)_2}$-(pyridine)	20,200	M→L CT	24
(benzene)-$\mathrm{Cr(CO)_2}$-(*trans*-4-styrylpyridine)[d]	16,340	M→L CT	24

[a] Acetonitrile solution, 300°K. [b] Rare gas matrices, 20°K. [c] Methanol solution, ambient. [d] Isooctane or other aliphatic hydrocarbon solution, ambient. [e] Benzene solution, ambient. [f] Ethanol solution, ambient. [g] phen = 1,10-phenanthroline.

states.[31] These one-electron excitations can result in dramatic changes in the substitutional lability of $\mathrm{M(CO)_6}$ since *both* σ-bonding and π-bonding are diminished by *depopulation* of $t_{2g}(\pi_b)$ and *population* of $e_g(\sigma^*)$.[32]

Reducing the symmetry of the system from O_h to at least C_{4v} substitution to form $\mathrm{M(CO)_5(X)}$ complexes causes changes in the one-electron energy levels.[33] Since CO lies so high in the spectrochemical series[34] it is

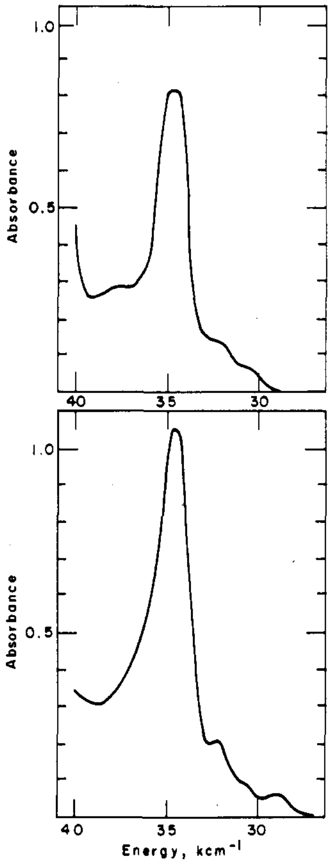


Figure 1. Electronic absorption spectra of 0.55 × 10^{-4} *M* $Mo(CO)_6$ (top) and 0.80 × 10^{-4} *M* $W(CO)_6$ (bottom) in EPA at 77°K. Note the presence of the band at 28,900 cm^{-1} in $W(CO)_6$ not observed in $Mo(CO)_6$ which is identified as the spin-forbidden ${}^1A_{1g} \rightarrow {}^3T_{1g}$ ($t_{2g}{}^6 \rightarrow t_{2g}{}^5e_g{}^1$) transition (ref 11); see Table II for extinction coefficients.

generally expected that substitution of CO to give $M(CO)_5(X)$ will result in a one-electron energy ordering like that shown in Scheme II. Naturally, if the LF treatment is to hold, the splitting of b_1 and a_1 should depend on the ligand X, and experimentally this is verified by noting (Table II) that the first absorption band is sensitive to the nature of X, but for ligands having the same donor atom the first band is at about the same energy even though the ligand, X, may or may not have a low-lying excited state of its own; *cf.* acetone *vs.* ether and NH_3 *vs.* pyridine. For the available data the spectrochemical series is

$$CO > \text{alkene} \sim PPh_3 > \text{pyridine} \sim \text{amine} \sim \text{oxygen-donor} \xleftarrow{\quad} 10Dq$$

For $W(CO)_5$(1-pentene) the first band appears at ~27,780 cm^{-1}, while for $W(CO)_5(NH_3)$ the corresponding band occurs at ~24,875 cm^{-1}. Thus, for the complexes studied, NH_3 and alkenes represent the extremes, consistent with alkenes being good π-acceptor ligands and amines being only σ-donor ligands. The one-electron energy levels in $W(CO)_5$(1-pentene) are not substantially different from those in $M(CO)_6$, while for $W(CO)_5(NH_3)$ the splitting of b_1 ($\sigma_{xy}*$) and a_1 (σ_z*) is enough to yield "localized" antibonding character along the *x* and *y* axes or the *z* axis depending upon the excitation energy. As with the O_h complexes the C_{4v} complexes exhibit an intense singlet → triplet LF band only for the W species. In Figure 2 a comparison of the low-energy absorptions for $Mo(CO)_5$(diethylamine) and $W(CO)_5$(diethylamine) is shown. Generally, the spectral features of $M(CO)_5X$ are qualitatively similar to those for other d^6, C_{4v} complexes.[35] The lowest energy transition[16-18] is the ${}^1A_1(e^4b_2{}^2) \rightarrow {}^{1,3}E(e^3b_2{}^2a_1{}^1)$, but higher energy excitations have not been assigned. Higher energy excitations should populate both M→L CT and LF states.

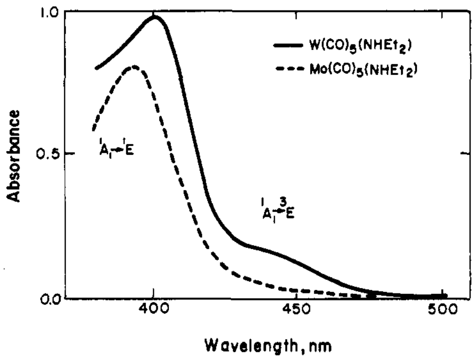


Figure 2. Electronic absorption spectra of $W(CO)_5(NHEt_2)$ (——) and $Mo(CO)_5(NHEt_2)$ (- - - -) in aliphatic hydrocarbon solution. The intense band ($\epsilon \cong 5000$) in the vicinity of 400 nm is identified as the ${}^1A_1 \rightarrow {}^1E$ ($e^4b_2{}^2 \rightarrow e^3b_2{}^2a_1{}^1$) spin-allowed transition and the shoulder only observed for the tungsten complex is the corresponding spin-forbidden ${}^1A_1 \rightarrow {}^3E$ transition (ref 16 and 17).

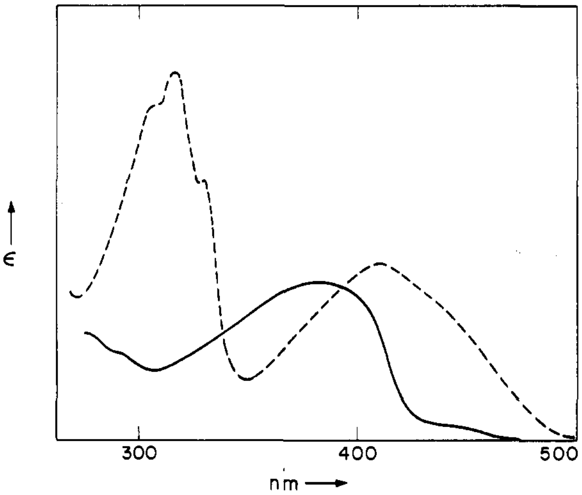
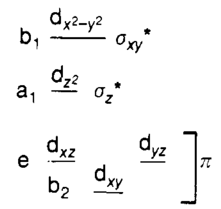


Figure 3. Comparison of electronic absorption spectra of $W(CO)_5$(pyridine) (——) and $W(CO)_5$(*trans*-4-styrylpyridine) (---). See Table I for extinction coefficients.

SCHEME II



The C_{4v} $M(CO)_5$ compounds have been studied in low-temperature matrices,[12] and the position of the first absorption band is consistent with a LF interpretation. The band position is even lower than with nitrogen or oxygen donors since there is no ligand in the sixth coordination site. It is clear, though, that the LF splitting will be dominated by $M(CO)_5$ when X is a weak field ligand in $M(CO)_5X$ since the $M(CO)_5$ spectra are not dramatically different from the $M(CO)_5$(amine) spectra, particularly for M = W or Mo.

The $M(CO)_5$(styrylpyridine) illustrates a situation where an intraligand transition obtains.[20] In Figure 3 we show a comparison of the absorption of $W(CO)_5$(pyridine) and $W(CO)_5$(*trans*-4-styrylpyridine). In the vicinity of 33,000 cm^{-1} the styrylpyridine complex exhibits an intense absorption with vibrational structure characteristic of the *trans*-stilbene-like chromophore. The red-shifted $^1A_1 \rightarrow {}^{1,3}E$ absorption in the styrylpyridine complex may reflect some contribution from a M→L CT absorption.

A final class of C_{4v} complexes merits attention. The "carbene" complexes $M(CO)_5C(OC_2H_5)R$ have low-lying absorption[27] near that for the $M(CO)_5$(amine) complexes, and the assignment of the lowest transition as the $^1A_1 \rightarrow {}^{1,3}E$ is attractive. However, a carbon donor is usually found high in the spectrochemical series. If the LF assignment is correct, the fact that the first band is at such low energies reveals that the carbene is surprisingly weak in LF strength. The M→L CT assignment is, thus, possible here.

Disubstituted complexes $M(CO)_4(X)_2$ have also been investigated. Data for only the cis geometry are available, and the lowest energy bands are again given the LF assignments. The lowering of the energy for the first LF band (compared to $M(CO)_6$) in *cis*-$M(CO)_4(X)_2$ should be only slightly more than that of $M(CO)_5(X)$, while the shift for *trans*-$M(CO)_4(X)_2$ should be substantially larger.[33a,35b,36] This fact may be used to rationalize differences in *trans*- and *cis*-$M(CO)_4X_2$ complexes. For example, *cis*-$Mo(CO)_4(PEt_3)_2$ is colorless while the trans isomer is yellow.[37] The data for amine complexes in Table II strongly support the notion that the first band in *cis*-$M(CO)_4(X)_2$ and $M(CO)_5X$ should occur at similar energies, and the lowest bands have been assigned as LF.[21,22] Only the W complexes exhibit the familiar shoulder associated with the lowest singlet → triplet absorption. Like the $M(CO)_6$[11] and many $M(CO)_5(X)$ complexes, the bands for *cis*-$M(CO)_4(X)_2$ exhibit only a very modest solvent dependence.[22] For the $M(CO)_4$(phenanthroline) complexes though, a very large solvent effect on the first transition is observed.[22] The lowest energy absorption band in these cases is identified as the $M \rightarrow L\pi^*$ CT band with LF transitions appearing only as shoulders at higher energy. The *cis*-$M(CO)_4$(pyridine)$_2$ spectra[20] more closely resemble the $M(CO)_4$(ethylenediamine) spectra, rather than the $M(CO)_4$(phenanthroline) spectra.[21,22]

The (arene)$M(CO)_3$ complexes represent a final mononuclear system where some effort has been directed toward understanding electronic structural features. These complexes were recognized early[25] as having an absorption band in the vicinity of ~38,500 cm^{-1} which was said to be characteristic of the M–C bond in metal-carbonyl-sandwich compounds. This band was later assigned as the $M \rightarrow \pi^*CO$ CT absorption, while the lower energy absorption maximum in the vicinity of ~31,000 cm^{-1} is assigned as a M→arene CT.[23] Some qualitative evidence in support of such an assignment can be gained by examination of the colors of the (arene)$M(CO)_3$ complexes.[38] For example, (benzene)$Cr(CO)_3$ is yellow, (*trans*-stilbene)$Cr(CO)_3$ is red, and (anthracene)$Cr(CO)_3$ is violet-black. The energy of the onset of absorption in these compounds seems to be related to the energy of the first $\pi \rightarrow \pi^*$ absorption[39] in the arene group. Further, (*cis*-stilbene)$Cr(CO)_3$ is only yellow while the *trans*-stilbene complex is red, again consistent with the ordering of the arene $\pi \rightarrow \pi^*$ energies.[39] Little work has been carried out with the Mo and W complexes, but examination of a published spectrum[26] of (hexamethylbenzene)-$W(CO)_3$ reveals enhanced absorption in the ~25,000 cm^{-1} region, perhaps reflecting the importance of direct singlet → triplet absorption due to the large spin-orbital coupling associated with the central metal. Finally, one may suspect that LF absorption is important on the low-energy side of the M→arene CT band in (benzene)$M(CO)_3$ since this is the region of the lowest LF bands in $M(CO)_6$.[11]

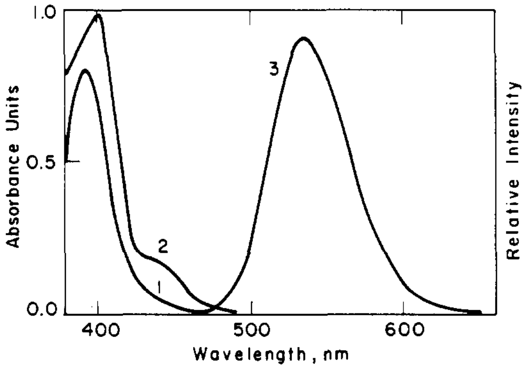


Figure 4. Electronic absorption spectra of $Mo(CO)_5$(cyclohexylamine) (curve 1) and $W(CO)_5$(cyclohexylamine) (curve 2) in aliphatic hydrocarbon solution and emission spectrum (curve 3) of the tungsten complex at 77°K. The molybdenum complex exhibited no luminescence (ref 16 and 17).

The monosubstituted complexes (arene)$Cr(CO)_2(X)$ are often highly colored with the first absorption energy being very sensitive to the ligand X. The ~4000-cm^{-1} red shift by changing X from pyridine to *trans*-4-styrylpyridine is consistent with a $M \rightarrow X\pi^*$ CT absorption. Even for X = acetylenic group the complexes are highly colored,[40] reflecting the ease of the M→L CT absorption in these systems. One expects relatively low energy M→L CT in these systems because only two CO groups remain coordinated to the central metal to accept electron density and stabilize the low oxidation state. In this regard we note that (arene)$Cr(CO)_2X$ complexes for X = σ-donor, π-donor are not particularly stable.

C. Luminescence Studies

Only a few papers dealing with luminescence of Cr, Mo, and W carbonyls have been published. It was found[16,17] that complexes of the formula $W(CO)_5(X)$, where X is an *n*-electron donor, will luminesce at 77°K either as the pure solid or in rigid glasses. The corresponding Cr and Mo complexes did not luminesce, or, at least, emission was not detectable under conditions used to determine spectra for the W complexes. The typical, structureless emission of $W(CO)_5(X)$ is exemplified in Figure 4. The lack of luminescence of the Cr and Mo complexes was correlated with the lack of an identifiable $^1A_1(e^4b_2^2) \rightarrow {}^3E(e^3b_2^2a_1^1)$ transition in absorption (*cf.* Table II). Emission maxima, lifetimes, and some relative yields are set out in Table III for some $W(CO)_5(X)$ complexes. Since the emission overlaps the low-energy absorption band and the lifetime is ~10^{-6} sec, it seems reasonable that the emission be assigned as the $^3E(e^3b_2^2a_1^1) \rightarrow {}^1A_1(e^4b_2^2)$ transition. Microsecond lifetimes are fairly typical of heavy transition metal complexes for spin-forbidden emission.[41-44]

The emission quantum yield, Φ_e, and the emission lifetime, τ_e, are related using eq 6 and 7. Using the Einstein

$$\tau_e = \frac{1}{k_{\text{nonradiative}} + k_{\text{radiative}}} \tag{6}$$

$$\Phi_e = \frac{k_{\text{radiative}}}{k_{\text{nonradiative}} + k_{\text{radiative}}} \tag{7}$$

equation,[45] the radiative rate constant can be estimated from the integrated absorption to the state from which emission occurs. Since the absorptivity only changes by

TABLE III. Luminescence of Tungsten and Molybdenum Carbonyl Derivatives

A. C_{4v} Complexes[a]

Complex	Emission max, nm	Rel Φ_e	$\tau_e \times 10^6$, sec
$W(CO)_5$	533		
$W(CO)_5(EtNH_2)$	533		0.92
$W(CO)_5(t\text{-}BuNH_2)$	533		1.2
$W(CO)_5(i\text{-}PrNH_2)$	533		0.65
$W(CO)_5(c\text{-}HxNH_2)$	533	1.0	1.1
$W(CO)_5(Et_2NH)$	533	6.0	5.1
$W(CO)_5(Me_2NH)$	533		2.6
$W(CO)_5$(piperidine)	533		3.1
$W(CO)_5(Et_2NMe)$	533		25.5
$W(CO)_5(Et_3N)$	533		9.7
$W(CO)_5(n\text{-}Bu_3N)$	533		6.9
$W(CO)_5(Me_2NCH(CH_3)Ph)$	533	12.0	15.5
$W(CO)_5(EtOH)$	~535		11.7
$W(CO)_5(i\text{-}PrOH)$	~535		6.6
$W(CO)_5(t\text{-}BuOH)$	~535		6.3
$W(CO)_5(Et_2O)$	533		7.1
$W(CO)_5$(acetone)	538		5.3
$W(CO)_5$(acetone-d_6)	~535		5.7
$W(CO)_5$(cyclohexanone)	~535		3.6
$W(CO)_5$(pyridine)	510		2.5
$W(CO)_5$(2-methylpyridine)	~520		1.7
$W(CO)_5$(2,4,6-trimethylpyridine)	~520		11.7

B. C_{2v} Complexes[b]

Complex	Emission max, $cm^{-1} \times 10^{-3}$ EPA, 77°K	Emission max, $cm^{-1} \times 10^{-3}$ Solid, 298°K	$\Phi_e \pm$ 20%[c]	$\tau_e \times 10^6$, sec
$Mo(CO)_4$(2,2′-bipyridine)		14.95		
$Mo(CO)_4$(1,10-phenanthroline)	16.08	15.45	0.087	11.6
$Mo(CO)_5$(5-methyl-1,10-phenanthroline	15.62	15.16	0.081	13.2
$Mo(CO)_4$(5-chloro-1,10-phenanthroline)	15.10	14.66	0.035	13.3
$W(CO)_4$(2,2′-bipyridine)		14.70		
$W(CO)_4$(1,10-phenanthroline)		14.84	0.054	11.6
$W(CO)_4$(5-methyl-1,10-phenanthroline)	15.31	14.93	0.036	12.5
$W(CO)_4$(5-chloro-1,10-phenanthroline)	14.82	14.83	0.022	7.9
cis-$W(CO)_4(n\text{-}PrNH_2)$	18.52	*d*		0.85
cis-$W(CO)_4$(piperidine)$_2$	18.35	*d*		28.5
cis-$W(CO)_4$(pyridine)	18.32	*d*		48.3
$W(CO)_4$-(ethylenediamine)	18.31	*d*		23.5

[a] References 16 and 17. Data for C_{4v} complexes are for methylcyclohexane solutions at 77°K. [b] Reference 49a. [c] Quantum yields measured in EPA at 77°K. [d] Not detectable.

small amounts while emission lifetimes vary over a wide range, large changes in $k_{\text{nonradiative}}$ are implicated for the $W(CO)_5(X)$ species. Unfortunately, these complexes do not luminesce in room-temperature fluid solution, clouding the relationship of the emission data and photoreactivity.

The luminescence data for the $W(CO)_5$(N-donor) (N-donor = NR_3, HNR_2, H_2NR) are particularly interesting. It is observed that for the H_2NR ligands the lifetime are grouped in the vicinity of 1×10^{-6} sec, HNR_2 complexes fall between 2.6 and 5.1×10^{-6} sec, and the NR_3 systems yield lifetimes in the range of $6.9\text{–}25.5 \times 10^{-6}$ sec. More hydrogens on the donor nitrogen yield the complexes having the shortest lifetimes and fastest rates of nonradiative decay. This effect is consistent with the general theory of Robinson and Frosch[46] which states that the highest energy vibrational modes in a molecule are the key to fast nonradiative decay. Removal of the high-energy N–H stretching modes in the series H_2NR, HNR_2, NR_3 thus reduces the rate of nonradiative decay. The fact that the N–H stretches seem to be particularly effective is reminiscent of the specific effect of replacing the α hydrogens in acetone with alkyl groups where it was found that nonradiative decay from both the singlet and the triplet state[47] is slowed by the loss of the C–H stretching modes. Finally, in this regard it is to be pointed out that for certain Cr(III) complexes[48] there seems to be a correlation of nonradiative decay rates and the number of high energy vibrational modes.

For the $W(CO)_5$(O-donor) complexes, importance of the O–H stretching mode as a nonradiative decay path is much less than in the N-donor cases. For example, the lifetime of $W(CO)_5(EtOH)$ is actually longer than the lifetime of $W(CO)_5(Et_2O)$. The explanation of this result requires further quantitative investigation of the relative emission quantum yields.

Optical luminescence has been recently observed[49] from a large number of bis-nitrogen donor tetracarbonylmolybdenum(0) and -tungsten(0) complexes. Data for these complexes of $\sim C_{2v}$ symmetry are included in Table III. For the complexes where the bis-nitrogen donor is 1,10-phenanthroline (and related ligands), both the Mo and W (but not Cr) species emit as solids at 298°K or in glassy solvents at 77°K. The position of the luminescence maximum correlates well with the position of the lowest $M \rightarrow \pi^*$ CT absorption. For complexes where the bis-nitrogen donor is an aliphatic amine or pyridine, luminescence was only detectable from the W species at low temperatures. The luminescence features of bis-aliphatic amine and -pyridine complexes parallels observations for the C_{4v} complexes, and thus, a LF triplet → singlet emission assignment is appropriate. The facts that for the 1,10-phenanthroline complexes room-temperature emission is seen, the Mo complexes emit, and the position of the band varies with the position of the lowest $M \rightarrow \pi^*$ CT absorption suggest a CT assignment for the luminescence in these complexes. The similar lifetimes and quantum efficiencies for the Mo and W species is seemingly inconsistent with a totally spin-forbidden transition.

D. Photoreactions

1. Substitution Reactions

a. $M(CO)_n(L)_{6-n}$ Complexes

Chemistry involving ligand exchange and substitution dominates the excited-state processes of $M(CO)_6$ complexes. It appears certain that the photochemical formation of $M(CO)_5(L)$ is obtained by the sequence outlined in eq 8–10. Several lines of evidence support very efficient generation of the coordinatively unsaturated intermediate, $M(CO)_5$, which has a substantial lifetime.

$$M(CO)_6 \xrightarrow{h\nu} M(CO)_5 + CO \qquad (8)$$

$$M(CO)_5 + CO \xrightarrow{k_9} M(CO)_6 \qquad (9)$$

$$M(CO)_5 + L \xrightarrow{k_{10}} M(CO)_5(L) \qquad (10)$$

It was found that a reversible photoreaction occurs upon photolysis of $M(CO)_6$ in a methyl methacrylate polymer.[50] The slow thermal bleaching of the yellow intermediate formed during photolysis is thought to be due to reaction 9. Infrared characterization of the $M(CO)_5$ intermediate was first gained by Sheline and coworkers[51] who obtained ir spectra after photolysis of $M(CO)_6$ at 77°K in methylcyclohexane glasses. The ir spectra supported assignment of the primary photoproduct as a C_{4v} $M(CO)_5$. However, evidence obtained upon thawing the $Mo(CO)_5$ sample implicated isomerization from a species of C_{4v} symmetry to one of D_{3h} symmetry. Strohmeier and his colleagues advanced chemical evidence[52] supporting the mechanism in eq 8–10. The initial quantum yield of 1.0 for $M(CO)_5L$ formation was found to be independent of M (M = Cr, Mo, W) and L. If a substantial contribution to the substitution process is an associative mechanism, one expects a dependence on the entering group L. It should be emphasized, however, that the *lack* of an effect by the entering group is not itself conclusive proof of the dissociative mechanism.

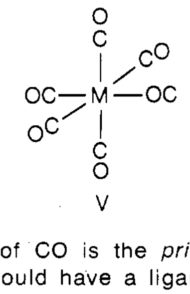
Later work by Turner and his associates has been carried out irradiating the group VI hexacarbonyls in low-temperature matrices.[12] Photolysis of $M(CO)_6$ in argon at 20°K yields the formation of $M(CO)_5$ having C_{4v} symmetry. Both ir and uv-visible spectral changes were monitored which appear to be consistent with the formation of C_{4v} $M(CO)_5$ which may subsequently thermally react with the photoreleased or added CO. In room-temperature fluid solutions, though, in the absence of any coordinating agent, species like IV are speculated[12] to exist. Such

$$(CO)_5M—OC—M(CO)_5$$

IV

an intermediate seems likely in light of the fact that the irradiated solutions of $M(CO)_6$ have a persistent yellow color even when CO is bubbled through them. The yellow color, however, could be due to $M(CO)_5X$ where X is an impurity nucleophile in the solvent. An earlier suggestion[53] that N_2 could be weakly bound to $M(CO)_5$ is substantiated by results[12] of photolysis of $M(CO)_5$ in matrices of pure nitrogen or mixed argon–nitrogen at 20°K.

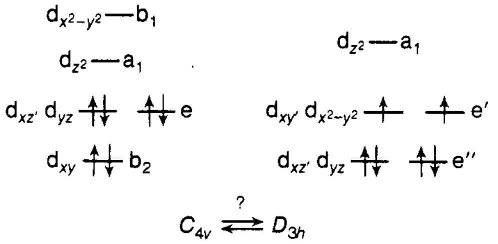
Flash photolysis of $M(CO)_6$ at room temperature has produced some conflicting conclusions. The first solution flash photolysis[54] indicated two intermediates which were identified as the C_{4v} and D_{3h} forms of $Cr(CO)_5$. Later work[55,56] led to the conclusion that the second intermediate is actually a $M(CO)_5(L)$ complex, where L is an impurity in the solvent, unreacted $M(CO)_6$, etc. None of the workers[54–57] agree on the absorption maximum in the uv-visible or the lifetime of the $Cr(CO)_5$, but it seems clear that an intermediate of this type is formed which is highly susceptible to attack by the poorest of nucleophiles. It is still possible that the isocarbonyl V, formed by linkage photoisomerization of CO is the *primary* photo product. The O-bound CO would have a ligand field strength like other oxygen donors such as ethers, alcohols, and ketones and is likely to be very weakly bound, decaying rapidly to the free $M(CO)_5$ intermediate by thermal dissociation.



V

The question of whether the $M(CO)_5$ is rigidly C_{4v}, D_{3h}, or easily interconvertible remains unresolved. One predicts a change in the d-orbital ordering like that indicated in Scheme III for a $C_{4v} \rightarrow D_{3h}$ conversion. One important physical property that undergoes a substantial change is the spin multiplicity. A d^6 configuration for the C_{4v} form is predicted to be diamagnetic, having a singlet ground state, while the D_{3h} form should have two unpaired electrons being a ground-state triplet. The likelihood that a triplet electronically excited state is responsible for loss of CO from $M(CO)_6$ makes the triplet ground state an attractive one since excited state decay would not be dampened by slow intersystem crossing. The large degree of spin-orbital coupling implicated by absorption data, however, makes such an argument of dubious value.

SCHEME III



Identification and characterization of the reactive excited state in $M(CO)_6$ complexes has not been pursued, probably because it suffices to say that the only decay path is dissociative loss of CO. The $M(CO)_6$ species have not been found to luminesce, and it is likely that spectroscopic excited states are extremely short-lived. The triplet-sensitized reaction of $Cr(CO)_6$ has been carried out,[58] and the reaction to yield loss of CO was found to be unity. The fact that the direct irradiation and triplet-sensitized yields are the same is consistent with decay of the excited states proceeding through a low-lying triplet state, but this point is clearly not proven. The $t_{2g}{}^6 \rightarrow t_{2g}{}^5e_g$ one-electron excitation in these systems gives rise to the ${}^1T_{1g}$, ${}^3T_{1g}$, ${}^1T_{2g}$, and ${}^3T_{2g}$ excited states, all of which should be substantially more reactive than the ground state, since depopulation of the t_{2g} level diminishes π-back-bonding and concomitant population of e_g diminishes σ-bonding *regardless* of the spin multiplicity of the excited state achieved. Our ability to resolve the question of relative reactivity of different spin states involved in these reactions may ultimately depend on our ability to observe the reactive state prior to its decay.

The synthetic utility of the sequence 8–10 has had considerable impact on systematic studies of chemical properties of the $M(CO)_n(L)_{6-n}$ complexes. From numerous early successes we conclude that derivatives of $M(CO)_6$ can be prepared by irradiation in the presence of almost any coordinating agent, L.[2–5] Our objective here is to attempt to generally account for the degree of substitution ultimately obtained, and how to control it. It was recognized from the outset that photolysis of $M(CO)_5L$ could result in the loss of another CO molecule (reaction 11) or loss of L (reaction 12).

$$M(CO)_5(L) \xrightarrow{h\nu} M(CO)_4(L) + CO \tag{11}$$

$$M(CO)_5(L) \xrightarrow{h\nu} M(CO)_5 + L \tag{12}$$

Reaction 11 leads to potentially two geometrical isomers of $M(CO)_4(L)_2$, and reaction 12 leads simply to ligand exchange in the presence of added L. The relative efficiencies of processes 11 and 12 were found to be very sensitive to the nature of L. In fact, for certain L, such as tetrahydrofuran (THF), process 12 is fairly insignificant, and nearly complete conversion of $M(CO)_6$ to $M(CO)_5(THF)$ can be achieved. The THF is weakly bound and a pure $M(CO)_5L$

TABLE IV. Wavelength Dependence for Quantum Efficiency of $M(CO)_5$(pyridine) to $M(CO)_4(pyridine)_2$ Conversion[a]

Central metal	Solvent	$\Phi_{366\ \mathrm{nm}}$	$\Phi_{436\ \mathrm{nm}}$
Cr	C_6H_6	0.21	0.13
Cr	THF	0.28	0.17
Mo	C_6H_6	0.16	0.11
Mo	THF	0.35	0.22
W	C_6H_6	0.11	0.08
W	THF	0.06	0.02

[a] References 60 and 61.

species is obtained by addition of L to the solution of $M(CO)_5(THF)$, reaction 13.

$$\mathrm{M(CO)_5(THF)} \xrightarrow[\mathrm{L}]{\Delta} \mathrm{M(CO)_5(L)} + \mathrm{THF} \qquad (13)$$

The relative importance of reaction 11 was found to increase with increasing strength of the M–L bond.[59] It is not obvious that such a correlation should exist since the excitation energies are high enough to yield loss of either the CO or L. If a common excited state is responsible for both reaction 11 and 12, the correlation could be rationalized by merely *assuming* that photoexcitation causes the same relative increase in substitution rate for L and CO. In such a case comparison of ground-state binding strength may yield the correlation observed: when L and CO are more comparable in binding strength release of CO is competitive with release of L, though in the ground state both undergo substitution slowly.

A second parameter was found to effect the relative efficiency of reactions 11 and 12. The reaction quantum yield for (11) was found to be sensitive to the wavelength of the exciting light as evidenced by data like those shown in Table IV.[60,61] Higher energy irradiation yields more efficient loss of CO. Such an effect can be attributed to at least two reactive excited states or to differences in the reactivity of one excited state depending on the vibrational level directly achieved. The latter alternative is not likely since the reactions are carried out in condensed media. Additional data,[20] Table V, reveals that both reaction 11 and 12 are wavelength dependent, with reaction 12 having attenuated importance upon higher excitation energy. The opposite wavelength dependence for the two processes can be rationalized by invoking two reactive LF excited states. The situation is detailed in Scheme IV. Low-energy excitation yields population of the d_{z^2} (σ_z^*) orbital with σ-antibonding character directed principally along the z axis strongly labilizing the σ donor, pyridine. Higher energy excitation populates the $d_{x^2-y^2}$ (σ_{xy}^*) orbital with strong labilizing effects for the equatorial CO's. Internal conversion of the upper state to the lower state with rate constant k_{nd} adequately accounts for the fact that reaction 12 occurs upon high-energy excitation. Impressive support of the rationale of the reactivity of $W(CO)_5$(pyridine) is found in the recent claim of selective incorporation of ^{13}CO into equatorial positions[62a] in $Mo(CO)_5$(piperidine) upon photolysis in the presence of ^{13}CO, and later similar evidence was obtained for the W analog.[62b]

SCHEME IV

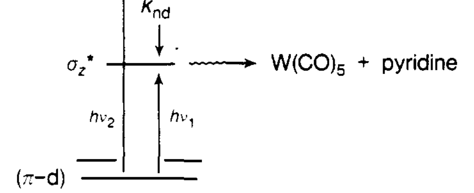


TABLE V. Wavelength Dependence for Processes 11 and 12 for M = W and L = Pyridine[a]

Irrdn, λ, nm	$\Phi_{\mathrm{eq}\ 11}$	$\Phi_{\mathrm{eq}\ 12}$
436	0.00_2	0.63
366	0.01_3	0.50
313	0.03_9	0.38
254	~0.04	0.34

[a] Quantum yields may depend on conditions used; *cf.* ref 20.

In Scheme IV the internal conversion associated with the rate constant k_{nd} is key to whether a wavelength-dependent reaction will obtain. In these cases we do find reaction from the upper state which means that k_{nd} is only competitive with the rate constant for chemical change. Consequently, modest changes in k_{nd}, say a factor of 5, will have a real bearing on the chemical reactions, and thus studies directed toward elucidating factors controlling k_{nd} should be quite fruitful.

The metal and solvent dependence on reaction 11 revealed by the data in Table IV are not easily explained. A clear explanation probably awaits results from reaction 12 and experiments designed to probe the point at which the solvent effect occurs.

Photolysis of $M(CO)_6$ has recently been used to produce tetra-, penta- and hexasubstituted derivatives (Table VI).[63-66] A combination of factors makes such highly substituted complexes possible including final product stability and the photolabilization of the CO at intermediate stages of substitution. All of the cases for which ML_6, $M(CO)L_5$, and $M(CO)_2L_4$ are found have L being a good π-acceptor ligand. That is, the loss of CO to yield stable low-valent complexes requires entering ligands capable of stabilizing the low-valent metal. Ligands having this quality should also tend to make possible the photolabilization of the CO. The substitution of CO by ligands which are like CO will not lead to substantial changes in the electronic structure, and thus, even though the symmetry may be quite low, the excited states are likely to be O_h-like. Consequently, CO photosubstitution can occur since the $t_{2g}^6 \rightarrow t_{2g}^5e_g$-type excitation is indiscriminate when all six ligands are good π acceptors. This situation is to be contrasted to situations like $W(CO)_5$(pyridine) where there are excited states which yield labilization of *either* the z axis or x-y axes. Empirically, for $W(CO)_5$(pyridine) z-axis excitation tends to preclude further CO substitution. Higher energy excitation yields more efficient loss of CO in $W(CO)_5$(pyridine) and the *cis*-$W(CO)_4(pyridine)_2$ is formed. Higher substitution involving entrance of principally σ-donor ligands is not common, perhaps, owing in part to the fact that for *cis*-$M(CO)_4(\sigma\ \mathrm{donor})_2$ there is only one remaining axis of the OC–M–CO type. Experiments to determine substitution yields of *cis*-$M(CO)_4(\sigma\ \mathrm{donor})_2$ are necessary to speculate further on this possibility; however, the stability of $M(CO)_n(\sigma\ \mathrm{donor})_{6-n}$ for $n \leq 3$ is likely to be relatively low.

b. (arene)$M(CO)_3$ Complexes

Two photosubstitution paths for (arene)$M(CO)_3$ complexes have been reported as generalized in eq 14[67] and 15.[68] The reaction quantum yield for (14) is in the vicinity of 0.80[24] for M = Cr, while that for (15) has not been reported. The high overall product yields for reaction 14 make the importance of (15) questionable. A selected

TABLE VI. Photosubstitution of Chromium, Molybdenum, and Tungsten Carbonyl by Ligands Capable of Stabilizing Low-Valent Metals

Starting complex	Entering ligand, L	Product(s)	Ref
$Cr(CO)_6$	(n-C_3H_7)OPF_2	CrL_6	63
	$P(OCH_3)_2F$	CrL_6	63
	$P(OCH_3)_3$	$Cr(CO)L_5$	63
		cis-$Cr(CO)_2L_4$	64
	$(CH_3)P(OCH_3)_2$	$Cr(CO)L_5$	63
	$(CH_3O)P(CH_3)_2$	$Cr(CO)L_5$	63
	$P(CH_3)_3$	*cis*-$Cr(CO)_2L_4$	64
$Mo(CO)_6$	PF_3	$Mo(CO)_5L$	65
		cis-$Mo(CO)_4L_2$	65
		trans-$Mo(CO)_4L_2$	65
		Isomers of $Mo(CO)_3L_3$	65
		cis-$Mo(CO)_2L_4$	65
		trans-$Mo(CO)_2L_4$	65
		$Mo(CO)L_5$	65
		MoL_6	65
	$P(OCH_3)_3$	MoL_6	63
	(n-C_3H_7O)PF_2	MoL_6	63
	$P(OCH_3)_2F$	MoL_6	63
	$P(CH_3)_3$	$Mo(CO)L_5$	63
		cis-$Mo(CO)_2L_4$	64
	$(CH_3)P(OCH_3)_2$	$Mo(CO)L_5$	63
$W(CO)_6$	$P(CH_3)_3$	*fac*-$W(CO)_3L_3$	64
		mer-$W(CO)_3L_3$	64
		cis-$W(CO)_4L_2$	64
		$W(CO)_4L_2$	64
		cis-$W(CO)_2L_4$	64
		$W(CO)L_5$	63
	$P(OCH_3)_3$	$W(CO)L_5$	63
		cis-$W(CO)_2L_4$	64
	(n-C_3H_7O)PF_2	WL_6	63
	$P(OCH_3)_2F$	WL_6	63
	$(CH_3)P(OCH_3)_2$	$W(CO)L_5$	63
	1,3-Butadiene	$Mo(CO)_2L_2$	66

list of recent examples of reaction 14 are given in Table VII.[69-75] At least for Cr it appears, as with $M(CO)_6$ (M = Cr, Mo, W), that photosubstitution can be achieved using

$$\text{(arene)M(CO)}_3 \xrightarrow[\text{L}]{h\nu} \text{(arene)M(CO)}_2\text{L} + \text{CO} \qquad (14)$$

$$\text{(arene)M(CO)}_3 \xrightarrow[\text{arene*}]{h\nu} \text{(arene*)M(CO)}_3 + \text{arene} \qquad (15)$$

almost any nucleophile as an entering group. This is not established for Mo and W (arene)$M(CO)_3$ complexes. In fact, it is claimed that (toluene)$W(CO)_3$ and (p-xylene)$W(CO)_3$ do not undergo CO exchange upon 254-nm excitation.[68]

In contrast to its thermal behavior[76] (cycloheptatriene)$Cr(CO)_3$ is found to yield substitution of CO upon 366-nm photolysis.[77] This comparison of ground and excited reactivity is like that found for (arene)$Cr(CO)_3$ which undergoes efficient arene group exchange upon heating.[78] *Dramatic differences in ground vs. excited state reactivity in each case may be ascribed to the fact that one-electron excitation is likely to change M–L binding more dramatically for a two-electron donor compared to the six-electron donor.*

TABLE VII. Photosubstitution Products of (arene)M(CO)$_3$

Initial complex	Entering ligand, L	Product	Ref
$(C_6H_6)Cr(CO)_3$	$[(Cp)FeC_5H_4]_3P$	$(C_6H_6)Cr(CO)_2L$	69
$(C_6H_6)Cr(CO)_3$	2,3-Diazabicyclo[2.2.1]-hept-2-ene	$(C_6H_6)Cr(CO)_2L$	70
$(CH_3OC_6H_5)Cr(CO)_3$	PPh_3	$(CH_3OC_6H_5)Cr(CO)_2L$	71
$((CH_3)_6C_6)Cr(CO)_3$	Cyclopentene, maleic acid, PhCCPh	$((CH_3)_6C_6)Cr(CO)_2L$	72
(mesitylene)-$Mo(CO)_3$	C_2H_4	(mesitylene)$Mo(CO)_2L$	73
$(CH_3C_6H_5)Mo(CO)_3$	^{13}CO	$(CH_3C_6H_5)Mo(CO)_2$ (^{13}CO)	74
$(C_6H_6)Cr(CO)_3$	Tetrahydrofuran	$(C_6H_6)Cr(CO)_2L$	75

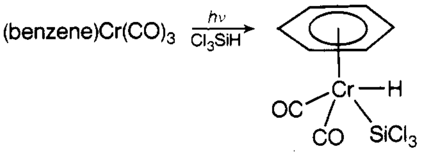
Reports of further loss of CO from (arene)$M(CO)_2L$ are not common. Thus, it is reasonable to conclude that excitation of this species leads to substitution lability of the ligand L. It has recently been demonstrated that reaction 16 proceeds to completion by irradiation with light of lower energy than 600 nm.[24] Process 16 exemplifies the potential photochromic properties of these systems with the styrylpyridine complex being dark blue while the pyridine complex is orange. Additionally, chemical systems which are sensitive to near-infrared light are not numerous, and new ones may merit evaluation as actinometric devices.

$$\text{(benzene)Cr(CO)}_2\text{(}\textit{trans}\text{-4-styrylpyridine)} \xrightarrow[\text{pyridine}]{\text{red light}} \text{(benzene)Cr(CO)}_2\text{(pyridine)} + \textit{trans}\text{-4-styrylpyridine} \qquad (16)$$

As with other metal carbonyls, the coordinatively unsaturated intermediates generated by photolysis of (arene)-$M(CO)_3$ can be involved as intermediates in redox reactions generally resulting in an oxidized central metal. Two examples are shown in reactions 17[79] and 18.[80] Nondestructive oxidative addition to the (benzene)-$Cr(CO)_2$ intermediate also appears to be possible as in reaction 19.[81]

$$\text{(arene)Cr(CO)}_3 \xrightarrow[\text{MeOH}]{h\nu} \text{Cr(OMe)}_3 + \text{arene} + 3\text{CO} \qquad (17)$$

$$\text{(arene)Cr(CO)}_3 \xrightarrow[\text{R}_2\text{S}_2]{h\nu} \text{Cr(SR)}_3 + \text{arene} + 3\text{CO} \qquad (18)$$



(19)

c. (Cp)M(CO)$_3$X Complexes

To date, very little mechanistic work has been carried out for complexes of this type, but several points can be made regarding the synthetic work carried out on these systems. The labilization of CO again appears to be the salient feature of the excited-state decay, and a high degree of substitution can be achieved as demonstrated by the photoproducts listed in Table VIII.[82-87] All three CO's can be substituted using a tridentate phosphorus donor. The restriction that the entering groups replacing CO be extremely good π-acceptor ligands may be relieved somewhat since the central metal in these cases is in either a +1 or +2 oxidation state. The loss of CO induced by photolysis can apparently be achieved regardless of X or the central metal, but the photolability of neither the cyclopentadienyl group nor X has been evaluated.

Work with these systems can be used to demonstrate other interesting consequences of CO lability. σ to π rearrangements like that in reaction 20 have been observed,[88,89] and the primary photoprocess is probably

$$\sigma\text{-3-C}_4\text{H}_3\text{SCH}_2\text{Mo(CO)}_3\text{(Cp)} \xrightarrow{h\nu} \pi\text{-2-C}_4\text{H}_3\text{SCH}_2\text{Mo(CO)}_2\text{(Cp)} + \text{CO} \qquad (20)$$

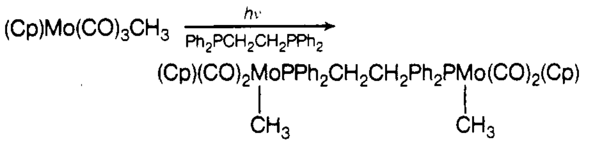
TABLE VIII. Photoproducts of (Cp)M(CO)$_3$X

Initial complex	Entering ligand, L	Product(s)	Ref
$C_3H_5Mo(CO)_2(Cp)$	Et_2NPF_2	$C_3H_5Mo(CO)(L)(Cp)$	82
$(Cp)Mo(CO)_3Cl$	$(Ph_2PCH_2CH_2)_2PPh$	$(Cp)Mo(L)Cl$	83
	PEt_3	$(Cp)Mo(CO)(L)_2Cl$	84
	$Ph_2PCH_2CH_2PPh_2$	$(Cp)Mo(CO)(L)Cl$	85
	$(Ph_2PCH_2CH_2)_2PPh$	$(Cp)Mo(CO)(L)Cl$	85
$(Cp)Mo(CO)_3I$	PEt_3	$(Cp)Mo(CO)(L)_2I$	84
	$P(OPh)_3$	$(Cp)Mo(CO)(L)_2I$	84
$[(Cp)Mo(CO)_2(diphos)]^+Cl^-$		$(Cp)Mo(CO)(diphos)(Cl)$	85
$[(Cp)Mo(CO)_3]_2$	$P(OC_6H_5)_3$	$[(Cp)Mo(CO)_2L]_2$	86
	PPh_3	$Cl_2Mo_2(CO)_5L$	87
$(Cp)Mo(CO)_3Sn(CH_3)_3$	$P(OC_6H_5)_3$	$(Cp)Mo(CO)_2(L)Sn(CH_3)_3$	86
$(Cp)Mo(CO)_3CH_3$	PPh_3	$(Cp)Mo(CO)_2(L)CH_3$	87
$(Cp)W(CO)_3CH_3$	PPh_3	$(Cp)W(CO)_2(L)CH_3$	87

dissociation of CO. Similar reactions also occur for the tungsten complexes,[90] reaction 21. Additionally, the

$$(\sigma\text{-}CH_2CHCH_2)W(CO)_3(Cp) \xrightarrow{h\nu} (\pi\text{-}CH_2CHCH_2)W(CO)_2(Cp) + CO \quad (21)$$

(Cp)M(CO)$_3$X systems can be used as examples of the formation of dinuclear metal carbonyls by coordination of two metals to a bidentate ligand as in reaction 22.[87]



$$(Cp)Mo(CO)_3CH_3 \xrightarrow[Ph_2PCH_2CH_2PPh_2]{h\nu} (Cp)(CO)_2\underset{\displaystyle CH_3}{\underset{|}{Mo}}PPh_2CH_2CH_2Ph_2P\underset{\displaystyle CH_3}{\underset{|}{Mo}}(CO)_2(Cp) \quad (22)$$

As indicated above, the relative importance of M–X bond cleavage has not been quantitatively investigated. However, reaction 23[91] demonstrates the necessity of evaluating this decay mode. Preliminary results[92] indicate that reaction 24 proceeds with high quantum efficiency ($\sim 10^{-1}$) upon either 546-nm or 366-nm irradiation with the stoichiometry shown.

$$[(Cp)Mo(CO)_3]_2 \xrightarrow[PPh_3]{h\nu} [(Cp)Mo(CO)_2(PPh_3)_2{}^+][(Cp)Mo(CO)_3{}^-] \quad (23)$$

$$[(Cp)M(CO)_3]_2 \xrightarrow[\substack{CCl_4 \\ \text{(degassed)}}]{h\nu} 2(Cp)M(CO)_3Cl \quad (24)$$

Substitution of CO in CpM(CO)$_2$(NO) can be achieved by irradiation[93] as in reaction 25. Additionally, products

$$(Cp)Mo(CO)_2(NO) \xrightarrow[PPh_3]{h\nu} (Cp)Mo(CO)(PPh_3)(NO), \quad (25)$$

which appear to arise from a nitrene intermediate are formed for M = Mo (eq 26). In the case of M = Cr only

$$(Cp)Mo(CO)(NO)(PPh_3) \xrightarrow[PPh_3]{h\nu} (Cp)Mo(CO)(NCO)(PPh_3)_2 + (Cp)Mo(CO)_2(PPh_3)(NCO) \quad (26)$$

simple substitution, reaction 25, is observed while for M = W the reactions like (26) obtain but give low yields. The nitrene mechanism gains some support from the fact that photolysis of an azido species gives similar product yields[93] (eq 27).

$$(Cp)Mo(CO)(PPh_3)_2(N_3) \xrightarrow{h\nu} (Cp)Mo(CO)(NCO)(PPh_3)_2 + (Cp)Mo(CO)_2(PPh_3)(NCO) \quad (27)$$

2. *Reactions of Coordinated Ligands*

Reactions of olefins which are accelerated by light in the presence of M(CO)$_6$ have received the most study. The reactions studied include cis–trans isomerization, double bond migration, hydrogenation, and dimerization. The role that light plays in these reactions is the point of interest here, and the following terminology is proposed. *Photocatalysis* is defined to be a situation *where light is used to generate a thermally active catalytic species,* and the reaction in question is, thus, not an excited-state transformation. In a photocatalytic reaction high quantum yields are expected, reaction may continue in the dark, after an initial irradiation period, and thermodynamic products are expected. *Photoassistance,* in contrast, is defined as a situation where the reaction requires binding the substrate to the metal, and the reaction is catalytic with respect to the metal, but *the reaction is not catalytic in photons.* In the photoassistance technique light plays a key role in one, two, or all of the following: (i) formation of the metal–substrate complex, (ii) transformation of the substrate, (iii) appearance of transformed substrate in the medium. Practically, the photoassistance technique requires continuous photolysis while in a photocatalytic reaction, after the catalyst has been generated, photolysis may no longer be necessary provided the catalytic transformation of the substrate is competitive with pathways for poisoning the catalyst. Naturally, *stoichiometric*

TABLE IX. Quantum Yields for Photoreactions of W(CO)$_5$X Complexes[a]

$$\text{(A) } W(CO)_5(py) \xrightarrow{h\nu} W(CO)_5(\text{1-pent})$$

$$\text{(B) } W(CO)_5(py) \xrightarrow{h\nu} cis\text{-}W(CO)_4(py)_2$$

$$\text{(C) } W(CO)_5(trans\text{-4-stypy}) \xrightarrow{h\nu} W(CO)_5(\text{1-pent})$$

$$\text{(D) } W(CO)_5(trans\text{-4-stypy}) \xrightarrow{h\nu} W(CO)_5(cis\text{-4-stypy})$$

$$\text{(E) } W(CO)_5(trans\text{-2-stypy}) \overset{h\nu}{\rightleftarrows} W(CO)_5(cis\text{-2-stypy})$$

$$\text{(F) } W(CO)_5(trans\text{-2-stypy}) \xrightarrow{h\nu} W(CO)_5(\text{1-pent})$$

Reaction	$\Phi_{436\ nm}$	$\Phi_{366\ nm}$	$\Phi_{313\ nm}$	$\Phi_{254\ nm}$
A[b]	0.63	0.50	0.38	0.34
B[c]	0.00_2	0.01_3	0.03_9	~0.04
C[b]	0.16	0.08	0.05	
D	0.49	0.34	0.26	0.21
E	0.08 ($t \rightarrow c$) 0.31 ($c \rightarrow t$)			
F[b]	0.16	0.07	0.13	

[a] Reference 20. py = pyridine; pent = pentene; stypy = styrylpyridine. [b] Φ measured at room temperature in the presence of 3.66 *M* 1-pentene–isooctane solvent. [c] Φ for formation of *cis*-W(CO)$_4$(py)$_2$ at room temperature in presence of 0.25 *M* pyridine in isooctane.

TABLE X. M(CO)$_6$ Photoassisted Reactions of Olefins

Metal complex used	Starting olefin	Product(s)	Ref
	A. Cis–Trans Isomerization		
W(CO)$_6$	*cis*-1,3-Pentadiene	*trans*-1,3-Pentadiene	94
	trans-1,3-Pentadiene	*cis*-1,3-Pentadiene	94
	trans,trans-2,4-Hexadiene	*cis,trans*-2,4-Hexadiene	94
	cis,trans-2,4-Hexadiene	*cis,cis*-2,4-Hexadiene	94
		trans,trans-2,4-Hexadiene	94
	cis,cis-2,4-Hexadiene	*trans,trans*-2,4-Hexadiene	94
		cis-trans-2,4-Hexadiene	94
	cis-Stilbene	*trans*-Stilbene	95
	trans-Stilbene	*cis*-Stilbene	95
	trans-1,2-C$_2$H$_2$D$_2$	*cis*-1,2-C$_2$H$_2$D$_2$	96
	trans-2-Pentene	*cis*-2-Pentene	96
	cis-2-Pentene	*trans*-2-Pentene	96
	trans-3-Hexene	*cis*-3-Hexene	96
	cis-3-Hexene	*trans*-3-Hexene	96
Mo(CO)$_6$	*cis*-1,3-Pentadiene	*trans*-1,3-Pentadiene	96
	trans-Stilbene	*cis*-Stilbene	95
	cis-Stilbene	*trans*-Stilbene	95
	B. Hydrogen Shift Reactions		
W(CO)$_6$	1-Pentene	*cis*-2-Pentene	96
		trans-2-Pentene	96
	cis- or *trans*-2 pentene	1-Pentene	96
	1-Hexene	*trans*-2-Hexene	96
	cis-3-Hexene	*cis*-2-Hexene	96
		trans-2-Hexene	96
W(CO)$_6$	*trans*-3-Hexene	*cis*-2-Hexene	96
		trans-2-Hexene	96
	cis-1,4-Hexadiene	*cis,cis*-2,4-Hexadiene	96
	trans-1,4-Hexadiene	*cis,trans*-2,4-Hexadiene	96
		trans,trans-2,4-Hexadiene	96
	1,4-Pentadiene	*trans*-1,3-Pentadiene	96
		cis-1,3-Pentadiene	96
Mo(CO)$_6$	1-Pentene	*cis*-2-Pentene	96
	C. Hydrogenation		
Cr(CO)$_6$	2,3-Dimethyl-1,3-butadiene	2,3-Dimethyl-2-butene	97, 97
	1,3-Cyclohexadiene	Cyclohexene	97, 98
	trans-1,3-Pentadiene	*cis*-2-Pentene	98
	2-Methyl-1,3-butadiene	2-Methyl-2-butene	98
	trans,trans-2,4-Hexadiene	*cis*-3-Hexene	98
Mo(CO)$_6$	*trans*-1,3-Pentadiene	1-Pentene	98
		cis-2-Pentene	98
		trans-2-Pentene	98
	2-Methyl-1,3-butadiene	2-Methyl-2-butene	98
W(CO)$_6$	*trans*-1,3-Pentadiene	1-Pentene	98
	cis-1,3-Pentadiene	*cis*-2-Pentene	98
		trans-2-Pentene	98
	2-Methyl-1,3-butadiene	2-Methyl-2-butene	98
	D. Dimerization		
Cr(CO)$_6$	Norbornadiene	Dimers	
		exo-*trans*-exo	99
		exo-*trans*-endo	99
		endo-*trans*-endo	99

excited-state reactions of coordinated ligands by photolysis of the complexes are possible and could be the key step in a photoassisted substrate transformation. However, studies of the stoichiometric excited-state reactions of coordinated ligands have been all too few to establish fundamental principles.

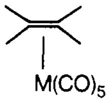
The stoichiometric reactions of coordinated ligands may occur *via* intramolecular energy migration from the coordination sphere to the ligand. An extreme case would be as indicated in VI where the excited states of the M(CO)$_5$ unit are noninteracting with the olefin. For olefins having low-lying excited states, electronic energy migration to produce olefin excited states may compete with

$$(CO)_5M\underset{\text{chain}}{\overset{\text{insulating}}{\sim\sim\sim\sim\sim}}\text{olefin}$$

VI

ligand substitution. The photoreactions of W(CO)$_5$(pyridine) and W(CO)$_5$(styrylpyridine) have been studied,[20] and the results may be interpreted in this manner even though no insulating group is present. The quantum yields for the various reactions are set out in Table IX. The data demonstrate that photosubstitution of the pyridyl group can be attenuated by the provision of another chemical decay path. The quantum yields for cis–trans isomerization of the 2- and 4-styrylpyridine seem to account for most of the loss in substitution yields. Further, for the 4-styrylpyridine the isomerization yields parallel substitution yields for the pyridine, implicating a similar excited-state precursor. It is probable that energy migration from $M(CO)_5$ to the styrylpyridine occurs largely from the lowest $^1A \rightarrow {}^1E$, ^3E states of the $M(CO)_5(X)$ unit.[20] These data provide one example of the potential usefulness of the energy which is normally "wasted" into ligand-exchange processes.

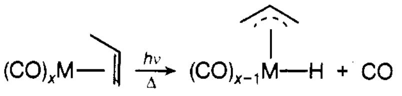
Direct coordination of olefinic linkages to the metal as in VII is common, and photolysis of solutions of alkenes,



VII

dienes, and other olefins in excess and catalytic amounts of Cr, Mo, and W carbonyls results in the olefin products detailed in Table X.[94-99] For the four types of reactions, only one generality seems reasonable at this time: *light plays a key role in forming reactive species including $M(CO)_n(olefin)_{6-n}$ and coordinatively unsaturated intermediates.* Beyond the formation of the olefin complexes little is known regarding details of the key steps in the actual olefin reaction. Some points of interest in this line are developed below.

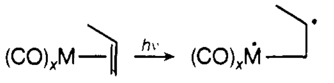
For the reactions involving simple alkenes isomerization, two intermediates seem possible. One (VIII) is the π-allylmetal hydride which could account for hydrogen shift products and cis–trans isomerization and could be formed either photochemically or thermally (eq 28). The π-allyl hydride could account for the observed photocatalysis.[96]



(28)

VIII

It is clear, though, that the π-allyl hydride will not account for the isomerization of 1,2-$C_2H_2D_2$. To account for this M–C σ-bonded olefin (IX) may be invoked (eq 29).



(29)

IX

An electronic energy migration mechanism is viewed as unlikely since the lowest alkene excited state (~80 kcal/mol)[100] is above the lowest $M(CO)_n$ LF states.[96] The 1,3-dienes probably react *via* intermediates similar to those for the simple alkenes, but the energy migration mechanism cannot be easily excluded since the lowest diene excited state is only 55 kcal/mol.[101] The stilbenes yield nonthermodynamic products by $M(CO)_6$ photoassisted isomerization.[95] The energy migration mechanism may obtain here, especially if coordination of the stilbene is through one of the phenyl rings.

The observation of only 2-hexenes from 1-hexene and 2-hexenes from the 3-hexenes reveals the requirement of sequential 1,3-hydrogen shifts to interconvert the 1- and 3-hexenes. Additionally, the 2-hexene product ratios starting with 1-hexene and *trans*-3- or *cis*-3-hexene are all different, implicating a different intermediate in each case.[96] The π-allyl hydride could account for this result provided it maintains some stereochemical integrity. The most consistent structure–reactivity relationship is that the activity for olefin reaction depends on the central metal in the order W > Mo ≫ Cr.[96] This effect may be ascribed, in part, to differences in the strength of metal–olefin binding. The W–olefin interaction is strongest, yielding a more significant olefin perturbation and hence a more reactive species.

TABLE XI. Spectral Data for Vanadium(—I) Hexacarbonyl[a]

Band position, cm^{-1}	ϵ	Assignment
43,750	73,700	
41,200	21,200	
37,550	60,900	$^1A_{1g} \rightarrow d^1T_{1u}$
~31,100	3,300	$^1A_{1g} \rightarrow {}^1T_{2g}$
28,400	6,240	$^1A_{1g} \rightarrow c^1T_{1u}$
25,100	1,640	Vibrational components of $^1A_{1g} \rightarrow {}^1T_{1g}$
23,200	300	

[a] Reference 11; room-temperature acetonitrile solution.

TABLE XII. Photosubstitution of Vanadium, Niobium, and Tantalum Hexacarbonyls[a]

Central metal	Entering ligand	Product
V	$P(OPh)_3$	$V(CO)_5(P(OPh)_3)^-$
	PPh_3	$V(CO)_5(PPh_3)^-$
	$Ph_2PCH_2CH_2PPh_2$	$V(CO_5(PPh_2CH_2CH_2PPh_2)^-$
	$AsPh_3$	$V(CO)_5(AsPh_3)^-$
	$SbPh_3$	$V(CO)_5(SbPh_3)^-$
	$P(n\text{-}C_4H_9)_3$	$V(CO)_5(P(n\text{-}C_4H_9)_3{}^-$
	$Ph_2PCH_2CH_2PPh_2$	$V(CO)_4(Ph_2PCH_2CH_2PPh_2)^-$
	$(Ph_2AsC_5H_4)_2Fe$	$V(CO)_4[(Ph_2AsC_5H_4)_2Fe]^-$
	2,2′-Bipyridyl	$V(CO)_4$(2,2′-bipyridyl)$^-$
Nb	PPh_3	$Nb(CO)_5(PPh_3)^-$
	$Ph_2PCH_2CH_2PPh_2$	$Nb(CO)_4(Ph_2PCH_2CH_2PPh_2)^-$
Ta	PPh_3	$Ta(CO)_5(PPh_3)^-$
	$Ph_2PCH_2CH_2PPh_2$	$Ta(CO)_4(Ph_2PCH_2CH_2PPh_2)^-$

[a] Reference 108b.

If one views the formation of IX as a reaction of electronically excited $M(CO)_5$ and an olefin, one can draw an interesting analogy with ground-state reactions of $Co(CN)_5{}^{3-}$. The d^7, C_{4v} $Co(CN)_5{}^{3-}$ has a single unpaired electron in the d_{z^2} orbital[102] and has radical-like properties including reactions with acetylenes and other olefins.[103] Excited $M(CO)_5$ would also have a single unpaired electron in the d_{z^2} orbital; thus we may rationalize the formation of the M–C σ-bonded olefin (IX).

The $Cr(CO)_6$ photoassisted dimerization of norbornadiene[99] is thought to proceed *via* photolysis of $Cr(CO)_4$(norbornadiene) which is a photosubstitution product. The ratio of dimeric products serves to reveal differences which may arise because of metal photoassistance compared to thermal pathways for reaction.

The recently reported $Cr(CO)_6$ photoassisted hydrogenation of 1,3-dienes[97] represents a vast improvement in the (arene)$Cr(CO)_3$ thermally catalyzed hydrogenation of dienes.[104] Neither elevated temperatures nor high H_2 pressures are required. Additionally, it is now known that a great deal of isomeric selectivity can be found for the photoassistance procedure.[98] For example, only *cis*-3-hexene is formed from *trans,trans*-2,4-hexadiene using $Cr(CO)_6$ as the catalyst. Further, the *trans,trans*-2,4-hexadiene is selectively hydrogenated from an equimolar mixture of the *trans,trans*- and *cis,cis*-2,4-hexadienes. This latter result typifies the selectivity of the catalyst for

TABLE XIII. Photosubstitution of (cyclopentadienyl)M(CO)$_n$(X)$_{4-n}$ Complexes[a]

Starting complex	Entering group, L	Product
(Cp)V(CO)$_4$	PhC≡CPh	(Cp)V(CO)$_2$L
(Cp)V(CO)$_3$PPh$_3$	PPh$_3$	(Cp)V(CO)$_2$PPh$_3$L
(Cp)V(CO)$_2$(PPh$_3$)$_2$	PhC≡CPh	(Cp)V(CO)(PPh$_3$)$_2$L
(Cp)V(CO)$_4$	1,3-Butadiene	(Cp)V(CO)$_3$L
(Cp)V(CO)$_4$	1,3-Cyclohexadiene	(Cp)V(CO)$_3$L
(Cp)V(CO)$_4$	2,3-Dimethylbutadiene	(Cp)V(CO)$_3$L
(Cp)Nb(CO)$_4$	PhC≡CPh	(Cp)Nb(CO)$_2$L
(Cp)(Nb(CO)$_3$PPh$_3$	PPh$_3$	(Cp)Nb(CO)$_2$PPh$_3$L
(Cp)Nb(CO)$_2$(PPh$_3$)$_2$	PhC≡CPh	(Cp)Nb(CO)(PPh$_3$)$_2$L
(Cp)Nb(CO)$_2$PhC≡CPh	PhC≡CPh	(Cp)Nb(CO)(PhC≡CPh)L
(Cp)Ta(CO)$_4$	PhC≡CPh	(Cp)Nb(CO)$_2$L

[a] Reference 109.

dienes which can easily achieve the s-cis conformation.[98] The apparent lack of total selectivity for the Mo and W carbonyls can be associated with their ability to isomerize the starting dienes and alkene products,[96] while Cr is ineffective in this regard. Finally, the Cr(CO)$_6$-H$_2$-light system has been shown to be truly photocatalytic with respect to hydrogenation of 1,3-dienes.[98]

III. Vanadium, Niobium, and Tantalum Carbonyls

A. Geometrical and Electronic Structures

The V, Nb, and Ta carbonyls have proven difficult to obtain but are known, and a new synthesis for them has recently been reported.[105] The d^6, M(−I) complexes are isoelectronic and isostructural with the Cr, Mo, and W carbonyls, and the V(CO)$_6^-$, Nb(CO)$_6^-$, and Ta(CO)$_6^-$ are found with a variety of cations. Derivatives are known, but little detailed information regarding electronic structure is available. The electronic spectrum of V(CO)$_6^-$ is similar to the spectrum reported for other d^6 M(CO)$_6$ systems. Band positions and spectral assignments are detailed in Table XI.[11]

For the anionic V, Nb, and Ta hexacarbonyls the ability of the CO to stabilize the low-valent central metal would seem to be more important than for Cr, Mo, and W since there is a full negative charge on the complex. This is borne out by comparing the CO stretching frequency for the anionic metal carbonyls with the neutral compounds.[106]

Interestingly, the natural d^5 V(CO)$_6$ compound also exists. In contrast to the yellow V(CO)$_6^-$ the d^5 compound is highly colored, absorbing throughout the visible spectrum, being a green-black compound. The lower energy absorption for the d^5 case could be due to the importance of L→M (t_{2g}) CT absorption since there is an unfilled t_{2g} level in d^5. In d^6 the t_{2g} level is filled and the next higher one-electron metal orbitals (e_g) are 10*Dq* above the t_{2g} set, implicating a substantially higher energy L→M CT transition. Similar arguments have been advanced to explain lower energy intense absorption in Fe(CN)$_6^{3-}$compared to Fe(CN)$_6^{4-}$.[107]

The complexes (cyclopentadienyl)M(CO)$_4$ (M = V, Nb, Ta) are formally seven-coordinate with the metal being in the +1 oxidation state. These complexes are thus "d^4," seven-coordinate systems like their Cr(II), Mo(II) and W(II) analogs (Cp)M(CO)$_3$(X).

B. Photoreactions

1. Hexacarbonyl Metalate(−I) Photoreactions

At the present time the excited-state chemistry associated with these carbonyl complexes is identified as substitution involving the CO groups.[108] In Table XII[108b] starting materials and substitution products are set out.

The anionic hexacarbonyls of V(−I), Nb(−I), and Ta(−I) undergo efficient loss of CO upon photoexcitation with uv light. No quantum efficiency data are available, but overall chemical yields are high. The substitution reactions of the anionic species represent the first direct incorporation of donor molecules into the coordination sphere of metal carbonyl anions *via* photolysis. However, the mechanistic implications are clouded by the note that reaction of the Ta(CO)$_6^-$ and Nb(CO)$_6^-$ with PPh$_3$ required temperatures of 40-60° to allow them to proceed at a measurable rate.

Intermediates during the substitution of bidentate ligands as in reaction 30 proved to be consistent with the

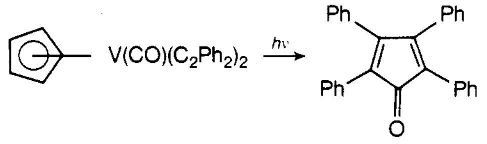
$$\mathrm{V(CO)_6^-} \xrightarrow[h\nu]{\mathrm{Ph_2PCH_2CH_2PPh_2\,=\,L}} \mathrm{V(CO)_4(L)^-} + 2\mathrm{CO} \qquad (30)$$

formation of a V(CO)$_5$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$^-$ which undergoes further loss of CO to yield the final product. Thus, as with the Cr, Mo, and W species the photolysis of M(CO)$_5$(X) yields loss of CO. It remains to be established whether X undergoes photosubstitution in the V(−I), Nb(−I), and Ta(−I) complexes.

While no detailed electronic spectral data are published for the photosubstitution products, the reported color changes for M(CO)$_6^-$ → M(CO)$_5$(X)$^-$ → *cis*-M(CO)$_4$(X)$_2^-$ seem appropriate for both a lowering of symmetry and of the average LF strength. The release of CO from the anionic hexacarbonyls is consistent too with the notion that transitions of the type t_{2g} → e_g diminish *both* π-back-bonding and σ-bonding of the CO groups. Indeed, since for the anionic carbonyls back-bonding should be most important, one may note the most impressive effects of depopulation of the t_{2g} level in these cases.

2. (cyclopentadienyl)M(CO)$_4$ Complexes

The photochemistry reported for these complexes again involves the substitution of CO. Reported photochemistry is detailed in Table XIII.[109] The primary photosubstitution of two CO's by acetylenes is unique, and it is curious that two acetylenes in the same molecule can apparently bind differently. One photochemical reaction is reported involving coordinated acetylenes and CO. The reaction is shown in eq 31, but no information regarding quantum efficiency is known.



(31)

TABLE XIV. Electronic Spectral Data for Manganese and Rhenium Carbonyls

Complex	Bands, cm^{-1} (ϵ)	Assignment	Ref
$[\mathrm{Mn(CO)_6}^+][\mathrm{BF_4}^-]^a$	49,900 (27,000)	$^1A_{1g} \rightarrow d^1T_{1u}$	11
	44,500 (16,000)	$^1A_{1g} \rightarrow c^1T_{1u}$	
	~39,600 (2200)	Vibrational components of	
	~37,300 (1100)	$^1A_{1g} \rightarrow {}^1T_{1g}$	
	~33,250 (600)	$^1A_{1g} \rightarrow {}^3T_{1g}$	
$[\mathrm{Re(CO)_6}^+][\mathrm{AlCl_4}^-]^a$	51,200 (77,900)	$^1A_{1g} \rightarrow d^1T_{1u}$	11
	47,100 (4600)	$^1A_{1g} \rightarrow {}^1T_{2g}$	
	44,500 (20,000)	$^1A_{1g} \rightarrow c^1T_{1u}$	
	40,700 (2900)	Vibrational components of	
	38,500 (1500)	$^1A_{1g} \rightarrow {}^1T_{1g}$	
	36,850 (708)	$^1A_{1g} \rightarrow {}^3T_{1g}$	
$\mathrm{CF_3Mn(CO)_5}^b$	~37,000 (~3000)	LF?	117
	~46,380 (30,000)	M→π*CO	
	>52,600 (>12,000)	M→π*CO	
$\mathrm{CH_3Mn(CO)_5}^b$	~35,500 (~3000)	LF?	117
	~45,050 (28,000)	M→π*CO	
	~51,020 (36,000)	M→π*CO	
$\mathrm{HMn(CO)_5}^b$	~30,000	LF?	117
	~33,000		
	37,000		
	47,280	M→π*CO	
	50,630	M→π*CO	
$\mathrm{ClMn(CO)_5}^c$	26,520 (600)	$^1A_1 \rightarrow {}^1E$	117
	37,000 (~1500)	LF?	
	45,050 (13,000)	M→CT	
	>52,600	X→π*CO	
$\mathrm{BrMn(CO)_5}^c$	26,070 (420)	$^1A_1 \rightarrow {}^1E$	117
	37,000 (1700)	LF?	
	43,950 (15,000)	M→π*CO	
	50,500 (7000)	X→π*CO	
$\mathrm{IMn(CO)_5}^c$	25,000 (360)	$^1A_1 \rightarrow {}^1E$	117
	33,600 (3000)	LF?	
	36,400 (1500)	LF?	
	42,700 (20,000)	M→π*CO, X→π*CO	
	52,630 (68,000)	M→π*CO	
$\mathrm{O_2NOMn(CO)_5}^d$	26,670 (1200)	$^1A_1 \rightarrow {}^1E$	118
$\mathrm{HRe(CO)_5}^b$	36,700	LF	117
	46,510	M→π*CO	
$\mathrm{ClRe(CO)_5}^d$	28,900	$^1A_1 \rightarrow {}^3E$	119, 120
	~31,350	$^1A_1 \rightarrow {}^1E$	
	~37,170	M→π*CO?	
$\mathrm{BrRe(CO)_5}^d$	28,490 (300)	$^1A_1 \rightarrow {}^3E$	119
	31,060 (2260)	$^1A_1 \rightarrow {}^1E$	
	33,220 sh	?	
$\mathrm{IRe(CO)_5}^d$	26,460 (200)	$^1A_1 \rightarrow {}^3E$	119
	29,670 (1990)	$^1A_1 \rightarrow {}^1E$	
	31,650 sh	?	
$[\mathrm{Mn(CO)_4Cl}]_2{}^b$	23,100 (~1000)	LF	117
	~29,400 (100–1000)	?	
$[\mathrm{Mn(CO)_4Br}]_2{}^b$	23,100 (2300)	LF	117
	~29,400 (700)	?	
$[\mathrm{Mn(CO)_4I}]_2{}^b$	22,800 (100–1000)	LF	117
	~28,600 (100–1000)		
$[\mathrm{Re(CO)_4Cl}]_2{}^b$	~27,000 sh	LF	120
$\mathrm{ClMn(CO)_3(NCCH_3)_2}^b$	26,600 (~1200)	LF	117b
$\mathrm{BrMn(CO)_3(NCCH_3)_2}^b$	26,500 (1500)	LF	117b
$\mathrm{ClMn(CO)_3(Et_2O)_2}^g$	25,000	LF	117b
$\mathrm{ClRe(CO)_4(pyridine)}^b$	~28,600 sh	LF	120
$\mathrm{ClRe(CO)_3(pyridine)_2}^e$	~29,400 sh	LF	120
$\mathrm{ClRe(CO)_3}$(5-methyl-1,10-phenanthroline)^e	~23,800 sh		120
	26,320 (4100)	M→Lπ*	
	37,310 (30,620)	Intraligand	
$\mathrm{ClRe(CO)_3}$(5-bromo-1,10-phenanthroline)^e	~24,050 sh	M→Lπ*	120
	25,840 (3900)		
	36,500 (27,500)	Intraligand	
$\mathrm{ClRe(CO)_3}$(5-nitro-1,10-phenanthroline)^e	~22,000 sh	M→Lπ*	120
	25,190 (3800)		
	36,630 (27,700)	Intraligand	
$\mathrm{C_5H_5Mn(CO)_3}^f$	30,390 (1120)		25

TABLE XIV (Continued)

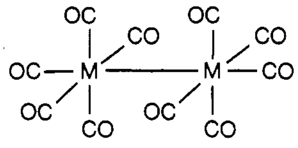
Complex	Bands, cm^{-1} (ϵ)	Assignment	Ref
$CH_3COC_5H_4Mn(CO)_3$^{f}	29,590 (1640)		25
$C_6H_5COC_5H_4Mn(CO)_3$^{f}	28,740 (2040)		25
(indenly)$Mn(CO)_3$^{f}	26,670 (1415)		25
$Mn_2(CO)_{10}$	29,400 (~20,000)	$\sigma_b \rightarrow \sigma^*$	121, 122
$Tc_2(CO)_{10}$	31,700	$\sigma_b \rightarrow \sigma^*$	121, 122
$Re_2(CO)_{10}$	32,300 (17,000)	$\sigma_b \rightarrow \sigma^*$	121, 122
$Mn(CO)_4(NO)$^{e}	23,360 (659)		123
$Mn(CO)_3(PPh_3)(NO)$^{e}	24,450 (694)		123
$Mn(CO)_3(AsPh_3)(NO)$^{e}	24,750 (696)		123

[a] CH_3CN, 298°K. [b] Cyclohexane, 298°K. [c] MeOH, 298°K. [d] $CHCl_3$, 298°K. [e] CH_2Cl_2, 298°K. [f] C_2H_5OH, 298°K. [g] Et_2O, 298°K.

IV. Manganese and Rhenium Carbonyls

A. Geometrical Structure

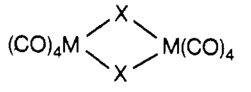
The commonly available carbonyls of Mn and Re have the formula $M_2(CO)_{10}$ with the structure shown in X. The



X

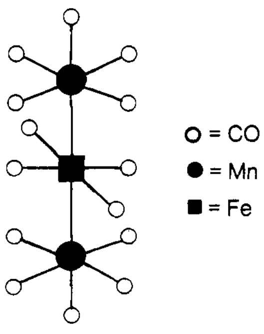
$M_2(CO)_{10}$ species are isostructural with $M_2(CO)_{10}^{2-}$ (M = W(−I), Mo(−I), Cr(−I)).[110] Aside from these $M_2(CO)_{10}$ compounds having zerovalent metals, six-coordinate M(I) compounds are known including $M(CO)_6^+$. Numerous substituted derivatives have been prepared including metal-carbonyl-alkyl compounds where it appears still appropriate to assign the +1 oxidation state to the central metal. The (Cp)$M(CO)_3$ complexes are stable and are again viewed as having the substitutionally inert d^6 electronic configuration.

A number of structurally interesting Mn and Re compounds are known to exist, and some are of importance with regard to discussion of excited-state processes. The species $M_2(CO)_8X_2$ (X = halogen) having structure XI[111]



XI

does not have a direct M–M bond. Heteronuclear metal carbonyls containing Mn and Re are fairly common and include $(CO)_5Mn\text{-}Re(CO)_5$,[112] $(CO)_4Co\text{-}Re(CO)_5$,[113] $[(CO)_5Re]_2Fe(CO)_4$,[114] and $[(CO)_5Re][(CO)_5Mn]Fe(CO)_4$.[115] The compound $Mn_2Fe(CO)_{14}$ has the structure XII.[116]



XII

B. Electronic Structure

Study of the electronic structure of Mn and Re carbonyls has been carried out for several different types of complexes. Absorption band positions, intensities, and likely assignments are set out in Table XIV.[11,25,117-123]

The spectra of the d^6 $Mn(CO)_6^+$ and $Re(CO)_6^+$ have strong similarity to the spectra of V(−I), Cr, Mo, and W carbonyls which have the same number of d electrons and are assigned accordingly. The lowest electronic transition is assigned as the $^1A_{1g}(t_{2g}^6) \rightarrow {}^3T_{1g}(t_{2g}^5e_g^1)$ LF absorption, and the other transitions are identified with bands found in the Cr, Mo, and W carbonyls. Replacing a CO by a ligand of weaker LF strength reduces the symmetry to at least C_{4v}. The striking similarity of the electronic spectra of $W(CO)_5$(piperidine) and $Re(CO)_5Cl$ is shown in Figure 5. Thus, though the prevailing literature[117,119] identifies the lowest bands as primarily CT in nature, it seems reasonable to assign the lowest bands in the $Re(CO)_5X$ and $Mn(CO)_5X$ compounds as the LF transitions $^1A_1 \rightarrow {}^{1,3}E$ as in the Cr, Mo, and W analogs. For the Mn and Re compounds the spectrochemical ordering seems to be consistent with other determinations of the series. As with the comparisons of Cr and W, the $Re(CO)_5X$ compounds appear to exhibit a more intense singlet → triplet absorption than the corresponding Mn compounds.

$$CO \sim H \sim \text{alkyl} \sim > \text{-}ONO_2^- > Cl^- > Br^- > I^-$$
$$\xleftarrow{\quad} 10Dq$$

The lowest absorption maximum for the dihalo-bridged compounds $M_2(CO)_8X_2$ appears to be consistent with an approximately *cis*-$M(CO)_4X_2$ chromophore. No trans-disubstituted complexes have been studied, but the shift in energy of the first electronic absorption from $M(CO)_5X$ to *cis*-$M(CO)_4X_2$ is expected to be small. The position of the first band in these compounds appears to follow the same spectrochemical ordering as in the $M(CO)_5X$ complexes. The *cis*-$ClRe(CO)_4$(pyridine) has its lowest electronic absorption band intermediate between $Re(CO)_5Cl$ and $[Re(CO)_4Cl]_2$ consistent with the known relative LF strengths of Cl^- and pyridine.

The donor atoms in the coordination sphere of $ClRe(CO)_3$pyridine)$_2$ are the same as those of $ClRe(CO)_3$(1,10-phenanthroline) but as seen in comparing Figures 6 and 7 the electronic spectra[120] of these two complexes are very different in the low-energy region. A similar relationship exists between *cis*-$M(CO)_4$(pyridine)$_2$ and $M(CO)_4$(1,10-phenanthroline) (M = Cr, Mo, W) with the 1,10-phenanthroline complex in each case exhibiting lower energy absorption which is assigned as the M→π* phenanthroline CT absorption. A comparison of the CT band position for the 5-methyl-, 5-bromo-, and 5-nitro-1,10-phenanthroline shows that the more electron-withdrawing substituents gives a lower energy band maximum consistent with the M→L direction of the CT excitation.

The lowest energy band maxima for several (Cp)$Mn(CO)_3$ complexes[25] are included in Table XIV, but

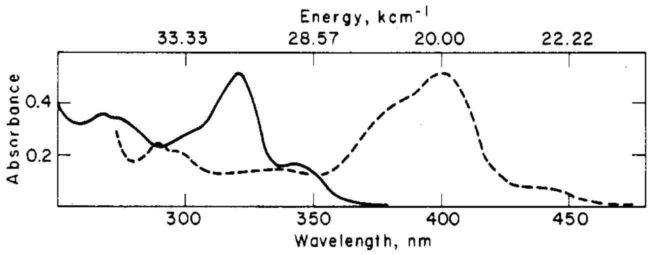


Figure 5. Comparison of electronic absorption spectra of $W(CO)_5$(piperidine) (----) and $Re(CO)_5Cl$ (——). Maximum ϵ at 405 nm for the former is ≈5000 and for the latter at 320 nm ≈2000.

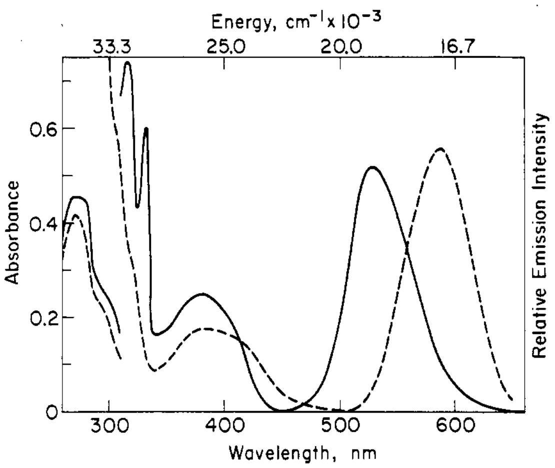
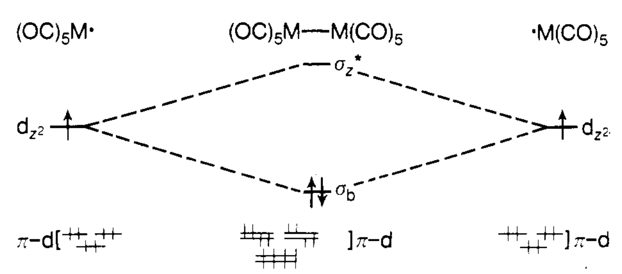


Figure 6. Absorption (left) and emission (right) at 298°K (---) and 77°K (——) of $ClRe(CO)_3$(1,10-phenanthroline) in EPA. Room-temperature absorption maxima are at 26,100 cm^{-1} (ϵ 4000) and 37,030 cm^{-1} (ϵ 30,600). Emission at 298 and 77°K were not recorded under the same sensitivity (ref 120).

detailed assignments have not been made. The sensitivity of the band positions to substitution in the ring implicates substantial M→π*(Cp) character.

The electronic spectra of the dimeric $M_2(CO)_{10}$ species are dominated by an intense (ϵ >10^4) absorption band in the vicinity of 31,000 cm^{-1}. This band is not present in the $M(CO)_6^+$ complexes, and energetic considerations[121,122] rule out a M→π*CO CT assignment. Assignment of the band as one associated with the M-M bond can be rationalized by a qualitative MO diagram (Scheme V).[121] The dimer can be viewed as being composed of two C_{4v} $M(CO)_5$ fragments of d^7 electronic configuration with the unpaired electron being in the d_{z^2} orbital. Overlap of the d_{z^2} orbitals forms the σ-bonding and σ-antibonding orbitals. As indicated in the diagram, the $M_2(CO)_{10}$ species is diamagnetic and should exhibit a $\sigma_b \rightarrow \sigma_z^*$ one-electron excitation. This transition associated with the M-M bond may be quite important in interpreting the photochemistry of the M-M bonded species (*vide infra*).

SCHEME V



The spectra of $M(CO)_5(X)$ (M = Mn, Tc, Re) can all be viewed in a similar fashion, but unless X = $M(CO)_5$ the relative orbital electronegativities will be different. Consider the MO diagram (Scheme VI) of $Mn(CO)_5CH_3$, where only σ interaction with the d_{z^2} orbital is shown. In these situations the $\sigma_b \rightarrow \sigma_z^*$ one-electron excitation is referred to as L→M CT. The [π-d] level is essentially noninteracting with regard to the $M-CH_3$ bond. The [π-d] → σ_z^* excitations are LF transitions, and their effect on bonding interactions has already been mentioned for the isoelectronic Cr, Mo, and W carbonyls. One notable point to be made here is that changes in reactivity upon LF or L→M CT excitation are due to the differences in the orbital, that is, *depopulated* since for both excitations the σ_z^* orbital becomes singly occupied.

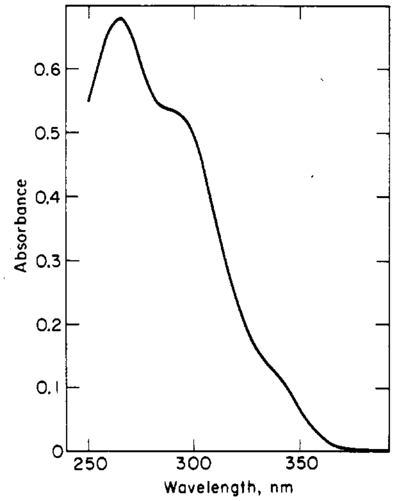
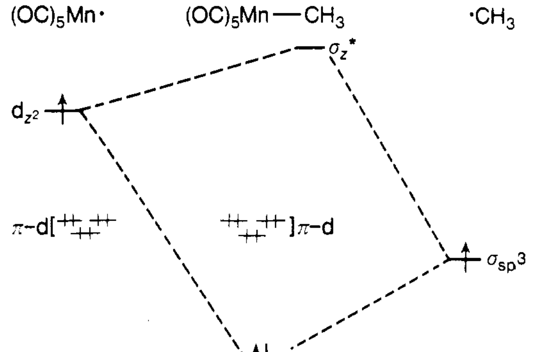


Figure 7. Absorption spectrum of 7.8 × 10^{-5} *M* $ClRe(CO)_3$(pyridine)$_2$ at 298°K in CH_2Cl_2 in a 1.0-cm path length (ref 120).

SCHEME VI



The complexes $Mn(CO)_3(X)NO$ (X = CO, PPh_3, $AsPPh_3$) are formally d^8 systems, isoelectronic with $Fe(CO)_5$. A low-energy band maxima is at higher energies for X = $AsPPh_3$ or PPh_3 than for X = CO.[123] Detailed interpretation is not possible without further study of this system.

C. Luminescence Studies

Only one series of Re carbonyl complexes have been reported to luminesce.[120] Generally, the $ClRe(CO)_3$(phenanthroline-X) complexes luminesce at either room temperature or below as solids, in fluid solutions, or in glassy media. The emission is at least partially spin-forbidden in nature as evidenced by lifetimes and quenching studies. Luminescence data for several complexes are outlined in Table XV.

Since the $ClRe(CO)_3(L)$ systems luminesce in fluid solution, this represents the first direct observation of the

TABLE XV. Luminescence Data for $\mathrm{ClRe(CO)_3(L)}$ Complexes[a]

L	Emission max, kcm⁻¹ 77°K	298°K	τ, sec × 10⁶ 77°K	298°K[b]	Φ ± 15% 77°K
1,10-Phenanthroline	18.94	17.33	9.6	0.3	0.33
2,2′-Bipyridyl	18.87		3.8	0.6	
5-Methyl-1,10-phenanthroline	18.83	17.01	5.0		0.33
4,7-Diphenyl-1,10-phenanthroline	18.18	17.24	11.25	0.4	
5-Chloro-1,10-phenanthroline	18.69	17.12	6.25		
5-Bromo-1,10-phenanthroline	18.69	17.09	7.6		0.20
5-Nitro-1,10-phenanthroline	18.28		11.8		0.03_3
1,10-Phenanthroline-5,6-dione	18.45		2.5		

[a] Reference 120; 77°K measurements in EPA; 298°K measurements in $\mathrm{CH_2Cl_2}$. [b] Deoxygenated solutions.

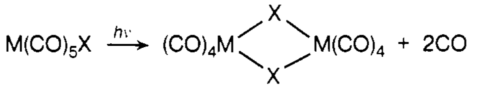
excited state of a metal carbonyl under conditions where photochemistry is normally carried out. The use of these as reagents for studies involving electronic energy transfer and nonradiative decay in solution has some promises. Intersystem crossing in these complexes measured by sensitized isomerization of *trans*-stilbene is very near unity as expected for systems involving a third row metal.[120] The order of magnitude decrease in lifetime at 298°K compared to the 77°K data is consistent with accelerated rates of nonchemical, nonradiative decay.

D. Photoreactions

1. Substitution Reactions

a. $\mathrm{M(CO)_n(L)_{6-n}}$ Complexes

No detailed studies of the photoreactions of the simple d^6 six-coordinate Mn, Tc, or Re carbonyls have been reported. However, several qualitative observations have appeared in the literature and merit attention here. It was recently found that reaction 32 proceeds photochemically.[117b,124] For the $\mathrm{Re(CO)_5Cl}$ the disappearance quantum yield at 313 nm is >0.50,[125] indicating that this reaction dominates all other excited-state pathways. It was pointed out that Mn–Cl cleavage to yield Cl does not obtain upon 436-nm photolysis of $\mathrm{Mn(CO)_5Cl}$ since $\mathrm{Mn_2(CO)_{10}}$ is not found when irradiation is carried out in the presence of 1 atm of CO.[117b] The lack of heterolytic M–Cl bond cleavage is consistent with the predicted[32] relative photolability of $\mathrm{Cl^-}$ *vs.* CO, the former being a π-donor and the latter a π-acceptor ligand. Higher energy excitation may yield L→M CT resulting in M–X cleavage.



(32)

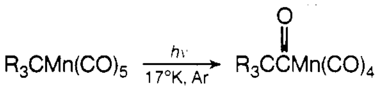
M = Mn M = Re
X = Cl, Br X = Cl, I

The photoreactions of a number of $\mathrm{Mn(CO)_5(L)}$ (L = strong σ-bonded ligand) complexes have been reported. Among these studies is the recent low-temperature photolysis of $\mathrm{Mn(CO)_5H}$ which undergoes loss of CO to form a five-coordinate species of trigonal-bipyramidal structure (reaction 33).[126] The regeneration of the $\mathrm{Mn(CO)_5H}$ by

$$\begin{tikzcd} \mathrm{Mn(CO)_5H} \arrow[r, "228\ \mathrm{nm}", "15°\mathrm{K,\ Ar}"'] & {[\mathrm{HMn(CO)_4} + \mathrm{CO}]} \arrow[l, bend left, "285\ \mathrm{nm}"] \end{tikzcd} \quad (33)$$

lower energy photolysis may be due to localized softening of the environment allowing thermal recombination of the coordinatively unsaturated intermediate and the ligand. The direct observation of the five-coordinate species does serve to establish the dissociative nature of the CO photosubstitution. Additionally, the implication of the trigonal-bipyramidal structure for $\mathrm{HMn(CO)_4}$ leads to the expectation that the stereochemical significance of photoproducts $\mathrm{HMn(CO)_4L}$ will be clouded. Interestingly, the photoinduced $^{13}\mathrm{CO}$ incorporation into $\mathrm{Mn(CO)_5Br}$ revealed no difference in the rate of axial *vs.* equatorial substitution, while the thermal reaction proceeded to give axial substitution at a rate equal to 0.74 times the equatorial rate.[127] These experiments provide support for different intermediates in the thermal and photosubstitution, but aside from this difference in reactivity no information is available regarding other properties of the intermediates with the exception that they are fluxional and five-coordinate.[127]

Irradiation of $\mathrm{R_3CMn(CO)_5}$ (R = H, D, F) at 17°K in an argon matrix has been shown to produce a five-coordinate acyl derivative (reaction 34).[128] The role of the light



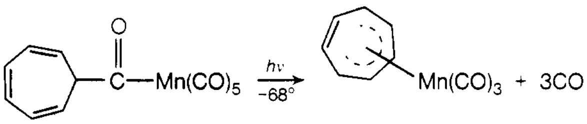
$$\mathrm{R_3CMn(CO)_5} \xrightarrow[17°\mathrm{K,\ Ar}]{h\nu} \mathrm{R_3C\overset{\overset{\displaystyle O}{\|}}{C}Mn(CO)_4} \quad (34)$$

R = H, D, F

in this reaction is not clear: is the primary process rupture of the Mn–$\mathrm{CR_3}$ or the Mn–CO bond?

The photolysis[129] of $\mathrm{(CO)_5Mn(\sigma\text{-}C_3H_5)}$ represents one of the earliest reports of a reorganization of bonding between the metal and the hydrocarbon group induced by photodissociation of CO (reaction 35). The decarbonylation reaction in (36) proceeds in 10.5% yield at −68°,[130] but the primary photoprocess is not obvious. Interestingly, the room-temperature photolysis yields only $\mathrm{Mn_2(CO)_{10}}$ and bitropyl, implicating $\mathrm{Mn(CO)_5}$ radical intermediates.

$$\mathrm{(\sigma\text{-}C_3H_5)Mn(CO)_5} \xrightarrow{h\nu} \mathrm{(\pi\text{-}C_3H_5)Mn(CO)_4} + \mathrm{CO} \quad (35)$$



(36)

Finally, with respect to the six-coordinate $\mathrm{M(CO)_n(L)_{6-n}}$ complexes, highly substituted derivatives of $\mathrm{Mn(CO)_5H}$ are formed *via* irradiation in the presence of $\mathrm{PF_3}$ (reaction 37).[131] The $\mathrm{PF_3}$ is, as usual in these cases, a strong π-acceptor ligand capable of stabilizing low oxidation states of the central metal.

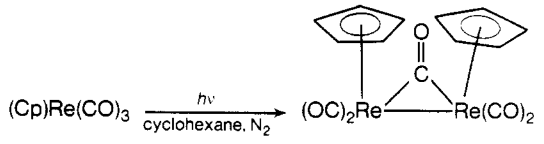
$$\mathrm{Mn(CO)_5(H)} \xrightarrow[\mathrm{PF_3}]{h\nu} \mathrm{HMn(CO)_n(PF_3)_{5-n}} \quad (37)$$

$n = 4, 3, 2, 1, 0$

b. $\mathrm{(Cp)M(CO)_3}$ Complexes

As with the $\mathrm{(arene)M(CO)_3}$ (M = Cr, Mo, W) complexes the dominant photoreaction of $\mathrm{(Cp)M(CO)_3}$ (M = Mn) is loss of CO, which leads to monosubstituted products (reaction 38). Most work has dealt with the first row Mn system though reaction 39[132] has been recently reported which is probably initiated by loss of CO. The

$$\mathrm{(Cp)Mn(CO)_3} \xrightarrow[L]{h\nu} \mathrm{(Cp)Mn(CO)_2L} + \mathrm{CO} \quad (38)$$



(39)

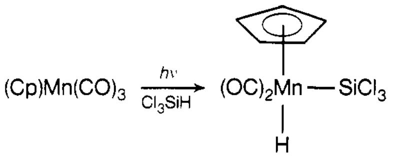
TABLE XVI. Photosubstitution Reactions of (Cp)Mn(CO)$_3$

Entering group, L	Product(s)	Ref
Tetrahydrofuran	(Cp)Mn(CO)$_2$L	134
(Ph$_2$PCH$_2$CH$_2$)$_3$N	(Cp)Mn(CO)L	135
(CH$_3$)$_2$NPF$_2$	(Cp)Mn(CO)L$_2$	82
C$_5$H$_{10}$NPF$_2$	(Cp)Mn(CO)L$_2$	82
2,3-Diazabicyclo[2.2.2]-hept-2-ene	(Cp)Mn(CO)$_2$L	70
Pyridine	(Cp)Mn(CO)$_2$L	136
Piperidine	(Cp)Mn(CO)$_2$L	137
SO$_2$	(Cp)Mn(CO)$_2$L	138
PPh$_3$	(Cp)Mn(CO)$_2$L (Cp)Mn(CO)L$_2$	139
1,3-Butadiene	(Cp)Mn(CO)L	140
Ethylene (other alkenes)	(Cp)Mn(CO)$_2$L	141
Benzene	(Cp)Mn(L)	142

quantum yield for (38) is 1.0 for L = acetone and diphenylacetylene[133] and presumably for other ligands as well. Again it is likely that (38) will proceed for any L having any nucleophilic character at all. This fact is demonstrated by the large number of examples in Table XVI.[70,82,134-142]

Further loss of CO from (Cp)Mn(CO)$_2$L has been observed in several cases notably for L = good π-acceptor ligand as evidenced by the examples given in Table XVI. All CO's have been displaced in the formation of (Cp)Mn(benzene).[142]

The coordinatively unsaturated intermediate from (Cp)Mn(CO)$_3$ is susceptible to oxidative addition like its (arene)Cr(CO)$_3$ analog (reaction 40).[81] The resulting



(40)

product is a distorted square pyramid and formally seven-coordinate.

Several examples of dinuclear complexes formed *via* photolysis in the presence of a bidentate ligand have been reported.[143-146] One typical example is shown in reaction 41. Photolysis of the dinuclear complex can result in the formation of the mononuclear (Cp)Mn(CO)L.[143] This may be the only example of a (Cp)Mn(CO)$_n$L$_{3-n}$ complex where the Mn-L is photolabilized, and even here it is possible that CO is lost first.

$$\text{(Cp)Mn(CO)}_3 \xrightarrow[\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2]{h\nu} \text{(Cp)Mn(CO)}_2\text{P(Ph}_2\text{)CH}_2\text{CH}_2\text{(Ph)}_2\text{PMn(CO)}_2\text{(Cp)} \quad (41)$$

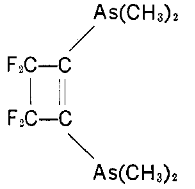
No one has claimed that substitution of the cyclopentadienyl ring is a primary photoprocess. Like with (arene)Cr(CO)$_3$ it is probable that the six-electron donor system is not labilized by a one-electron excitation to the degree of the two-electron donor CO groups. Finally, the only derivative of a substituted cyclopentadienyl that has been studied, (CH$_3$Cp)Mn(CO)$_3$, behaves like the parent species.[81,136,143,147]

c. Mn(CO)$_4$NO

The five-coordinate Mn(CO)$_4$NO complex is isoelectronic with Fe(CO)$_5$. LiKe Fe(CO)$_5$, the photoinduced loss of CO leads to a dinuclear carbonyl (reaction 42).[148]

$$2\text{Mn(CO)}_4\text{NO} \xrightarrow{h\nu} \text{Mn}_2\text{(CO)}_7\text{(NO)}_2 + \text{CO} \quad (42)$$

TABLE XVII. Photosubstitution Products of M$_2$(CO)$_{10}$

M	Entering group, L	Product(s)	Ref
Mn	PPh$_3$	Mn$_2$(CO)$_9$L	155
		Mn$_2$(CO)$_8$L$_2$	155–158
	P(OC$_6$H$_5$)$_3$ P(C$_2$H$_5$)$_3$ P(C$_6$H$_4$F)$_3$ As(C$_6$H$_5$)$_3$	Mn$_2$(CO)$_8$L$_2$	155
Re	PF$_3$	Re$_2$(CO)$_{10-n}$L$_n$	159
Mn	PF$_3$	Mn$_2$(CO)$_{10-n}$L$_n$ (n = 1, 2, 3)	159
Re	CH$_3$P(C$_6$H$_5$)$_2$	Re$_2$(CO)$_{10-n}$L$_n$ (n = 1, 2, 3)	160
Mn	^{13}CO	Mn$_2$(CO)$_n$(^{13}CO)$_{10-n}$	161
Mn	CH$_2$=CHCN C$_6$H$_5$CN CH$_3$CN	Mn$_2$(CO)$_9$L (equatorial)	162
Re, Mn		M$_2$(CO)$_8$L (bridging L)	163, 164

Low-temperature photolysis in an argon matrix has revealed formation of a coordinatively unsaturated species (reaction 43) which itself is photosensitive.[149] The

$$\begin{tikzcd}
\text{Mn(CO)}_4\text{NO} \arrow[r, "h\nu", "15^\circ\text{K, Ar}"'] & \text{Mn(CO)}_3\text{NO} + \text{CO} \arrow[l, bend left, "\Delta,\ 30^\circ\text{K}"] \arrow[d, "h\nu"', "15^\circ\text{K, Ar}"] \\
 & \text{Mn(CO)}_2\text{NO} + \text{CO} \quad (43)
\end{tikzcd}$$

Mn(CO)$_3$NO intermediate is presumably involved in the room-temperature photochemistry (reaction 42 or 44), to produce Mn(CO)$_3$L(NO) complexes.[123]

$$\text{Mn(CO)}_4\text{(NO)} \xrightarrow[\text{L}]{h\nu} \text{Mn(CO)}_3\text{(L)NO} + \text{CO} \quad (44)$$

$$\text{L} = \text{PPh}_3,\ \text{AsPh}_3,\ \text{P(}n\text{-Bu)}_3$$

Quantum yields for reaction 44 were less than unity and found to depend both on the entering group L and for PPh$_3$ its concentration.[123] These two facts were interpreted as indicative of an associative contribution to the dissociative path for substitution. Such a result may be reasonable if the nature of the Mn-NO interaction is changed photochemically such as a change from NO = three-electron donor to NO = one-electron donor.

2. *Photoactivation of the M-X Bond in Mn(CO)$_5$X*

A number of reports now exist revealing that the Mn-X bond can be cleaved by photolysis of Mn(CO)$_5$X for a wide variety of σ-bonded X groups including R$_3$Sn, R$_3$Ge, and alkyl. Examples have already been presented of a photoassisted carbonylation (reaction 34) and decarbonylation (reaction 36), but in these examples it is not clear that cleavage of the Mn-X bond is the primary excited-state decay path. The homolytic scission of Mn(CO)$_5$X to yield Mn(CO)$_5$ and X might be expected if high-energy excitation is used to ensure achievement of the σ_b-σ_z* (L→M CT) excitation.

Existing experimental reports lead to conflicting conclusions regarding the dominant primary photoreaction. The insertion reaction 45 is reported to go in essentially

$$\text{CH}_3\text{Mn(CO)}_5 \xrightarrow[\substack{h\nu \\ \text{1-2 atm}}]{\text{F}_2\text{C=CF}_2} \text{CH}_3\text{CF}_2\text{CF}_2\text{Mn(CO)}_5 \quad (45)$$

TABLE XVIII. Photoreactions of $M_2(CO)_{10}$ Involving Rupture of the M-M Bonds

Starting M-M bonded species	Added reagent(s)	Product(s)	Ref
$Mn_2(CO)_8$(1,10-phenanthroline)	Chlorinated solvent	$ClMn(CO)_3$(phen) + $ClMn(CO)_5$	165
$Re_2(CO)_{10}$	$Fe(CO)_5$	$(CO)_5M\text{-}Fe(CO)_4\text{-}M(CO)_5$ + $MnFe(CO)_{10}$	166
$Mn_2(CO)_{10}$	$Fe(CO)_5$		
$Tc_2(CO)_{10}$	$Fe(CO)_5$		
$Re_2(CO)_{10}$ + $Mn_2(CO)_{10}$		$ReMn(CO)_{10}$	115
$Mn_2(CO)_{10}$	HBr	$BrMn(CO)_5$	167
$Re_2(CO)_{10}$	CCl_4	$ClRe(CO)_5$	124a
$Mn_2(CO)_{10}$	CCl_4	$ClMn(CO)_5$	168, 169
$Mn_2(CO)_{10}$	I_2	$IMn(CO)_5$	169
$Re_2(CO)_{10}$	I_2	$IRe(CO)_5$	124b, 169
$(CO)_5Mn\text{-}Re(CO)_3$(phen)		$Mn_2(CO)_{10}$ + $[Re(CO)_3(phen)]_2$	170, 171

quantitative yield,[150] while simple substitution in reaction 46 gives good yields as well.[151] Additionally, reaction 47 goes smoothly, yielding simple substitution products.[131]

$$C_6F_5Mn(CO)_5 \xrightarrow[h\nu]{\text{pyridine}} C_6F_5Mn(CO)_4(\text{pyridine}) \quad (46)$$

$$HC_2F_4Mn(CO)_5 \xrightarrow[PF_3]{h\nu} HC_2F_4Mn(CO)_4PF_3 \quad (47)$$

However, aside from the insertion reaction in (45), other systems give varying ratios of insertion and what appear to be free radical coupling products. For example, consider the photoreactions of $(CH_3)_3GeMn(CO)_5$ in the presence of C_2F_4 and CF_3CFCF_2, reactions 48 and 49, respectively.[152] The analogous $(CH_3)_3SnMn(CO)_5$ undergoes no decomposition at 130°, but upon photolysis under conditions as for the $(CH_3)_3Ge$ compound rich chemistry is obtained[153] (reaction 50).

$$(CH_3)_3GeMn(CO)_5 \xrightarrow[F_2C=CF_2]{h\nu}$$
$$(CH_3)_3GeF + CH_3GeCF_2CF_2Mn(CO)_5 + Mn_2(CO)_{10} \quad (48)$$

$$\xrightarrow[\substack{CF_3CF=CF_2 \\ 50°,\ \text{pentane}}]{h\nu} Mn_2(CO)_{10} + CF_3CFCFMn(CO)_5 \quad (49)$$

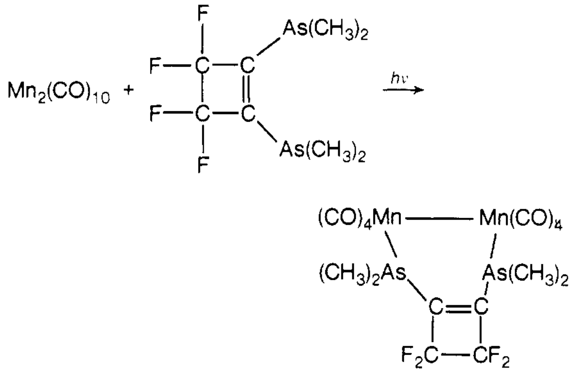
$$(CH_3)_3SnMn(CO)_5 \xrightarrow[F_2C=CF_2]{h\nu} C_5F_9Mn(CO)_5 +$$
$$(CH_3)_3SnCF_2CF_2Mn(CO)_5 + CF_2{=}CFCOMn(CO)_5 +$$
$$[CF_2{=}CFMn(CO)_4]_2 \quad (50)$$

It is therefore clear that photolysis can activate the Mn-X bond in $XMn(CO)_5$ complexes, and substantial activation of hydro- and fluorocarbons can be obtained.[152-154] However, answers to questions regarding structure-reactivity relationships are not yet available.

3. Photoreactions of $(OC)_{5-n}L_nM\text{-}M(CO)_{5-m}L'_m$ Complexes

The parent carbonyls of Mn and Re, $M_2(CO)_{10}$, may be viewed as special cases of $M(CO)_5X$ where X = $M(CO)_5$. As has already been pointed out, these complexes exhibit an intense electronic absorption band corresponding to a $\sigma_b \rightarrow \sigma_z{}^*$ transition associated with the metal-metal bond. Such one-electron transitions should substantially reduce the strong M-M interaction. Consistent with this notion are several qualitative reports which, by products alone, suggest that a large fraction of absorbed quanta result in declusterification, yielding mononuclear products. Contrary to these results are several claims that simple CO substitution occurs upon photolysis of $M_2(CO)_{10}$. Detailed examples of each of these are outlined below.

In Table XVII[155-164] we list simple CO substitution products obtained *via* photolysis of $Mn_2(CO)_{10}$ or $Re_2(CO)_{10}$. Generally, the incorporation of L proceeds stepwise, and L assumes either an axial position if it is a good π-acceptor or an equatorial position if L is a N-donor. A chelate ligand can bridge both metals as in reaction 51.[153,164] Substitution reactions of $M_2(CO)_{10}$ appear to occur with relatively modest efficiencies in contrast to other metal carbonyls and are often accompanied by "decomposition." However, no quantum yield information is available, and no one has determined the wavelength dependence of these reactions.



(51)

Photoproducts arising from rupture of the M-M bond in $M_2(CO)_{10}$ and related speices are set out in Table XVIII.[124,165-171] It has recently been determined that reaction 52 occurs with a quantum yield of 0.60 and with the stoichiometry shown.[124] Further, irradiation of $Mn_2(CO)_{10}$ in the presence of HBr gives a nearly quantitative yield of $Mn(CO)_5Br$[167] or $Mn(CO)_5Cl$ in CCl_4.[169] This quantum yield and stoichiometric data provide substantial evidence that a principal primary decay path is symmetrical cleavage of the M-M band followed by radical-like reactions of the resulting metal containing fragments. Other observations in support of such a decay path are the products indicated in Table XVIII. Unsymmetrical cleavage to yield $M(CO)_4$ and $M(CO)_6$ fragments[172] seems unlikely in view of these results.

$$Re_2(CO)_{10} \xrightarrow[CCl_4]{313\text{ nm}} 2Re(CO)_5Cl \quad (52)$$

The high quantum yield for $Re(CO)_5Cl$ formation from $Re_2(CO)_{10}$ in CCl_4[124a] indicates that CO dissociation is not as important as M-M bond cleavage. Aside from photodissociation of CO one may envision a substitution mechanism like that indicated in Scheme VII, where RX is an alkyl halide and L is a nucleophile. The mechanism

TABLE XIX. Uv-Visible Absorption Data for Iron, Ruthenium, and Osmium Carbonyls

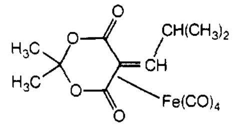
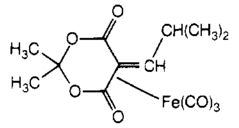
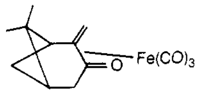
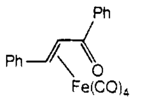
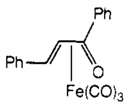
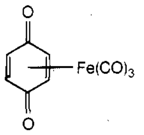
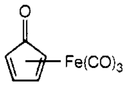
Complex	Bands, cm^{-1} (ϵ)	Ref
$Fe(CO)_5$	~35,500 (3800) ~40,000 (40,000)	25, 187
$Fe(CO)_4^{2-}$	33,000 (...)	188
$Fe_2(CO)_8^{2-}$	28,800 (8920)	188
$Fe_3(CO)_{11}^{2-}$	20,600 (3160)	188
$Fe_4(CO)_{13}^{2-}$	20,000 (4470)	188
	29,000 (1600) 41,000 (12,000)	189
	24,000 (520) 30,700 (2400)	189
	23,500 (550) 29,700 (1980) 42,200 (11,900)	190
	29,500 (5500) 32,500 (8600) 38,800 (22,400)	190
	29,000 (4400) 33,200 (13,200) 40,000 (22,800)	190
$[Fe(CO)_3Br]_2$	21,700 (900) 28,300 (7600)	191
$Fe(CO)_2I]_2$	19,500 (700) 27,400 (3200)	191
(1,3-butadiene)$Fe(CO)_3$	36,000 (2460) ~47,300 (23,000)	25
	28,400 (2820) 33,800 (2760) 37,900 (5900)	192
	29,400 (1780) 33,600 (5000)	192

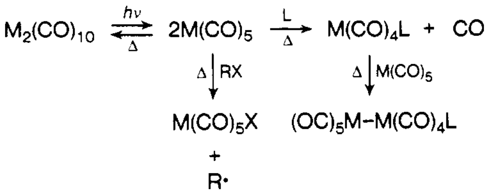
TABLE XX. Colors of the Carbonyls of Fe, Ru, and Os[a]

Complex	Color
$Fe(CO)_5$	Yellow
$Fe_2(CO)_9$	Orange
$Fe_3(CO)_{12}$	Black-green
$Ru(CO)_5$	Colorless
$Ru_3(CO)_{12}$	Orange-red
$Os(CO)_5$	Colorless
$Os_3(CO)_{12}$	Yellow
$[(Cp)Fe(CO)_2]_2$	Red-purple
$[(Cp)Ru(CO)_2]_2$	Orange-red
$[(Cp)Os(CO)_2]_2$	Yellow

[a] Reference 193.

outlined in Scheme VII depends upon the efficient scission of $M_2(CO)_{10}$ to yield d^7 $M(CO)_5$ species which may be thermally substitution labile. Subsequent coupling of $M(CO)_nL_{5-n}$ regenerates the M–M bond, while in the presence of an alkyl halide halogen atom abstraction may compete to yield $XM(CO)_nL_{5-n}$.

SCHEME VII



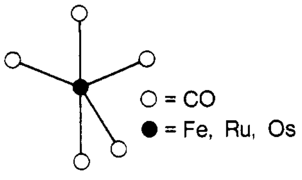
$$\begin{tikzcd} M_2(CO)_{10} \arrow[r, shift left, "h\nu"] & 2M(CO)_5 \arrow[l, shift left, "\Delta"] \arrow[r, "L", "\Delta"'] \arrow[d, "RX", "\Delta"'] & M(CO)_4L + CO \arrow[d, "M(CO)_5", "\Delta"'] \\ & M(CO)_5X + R\cdot & (OC)_5M\text{-}M(CO)_4L \end{tikzcd}$$

The *formation* of new cluster compounds can also be achieved by photolysis of $M_2(CO)_{10}$ in the presence of other metal carbonyls. Irradiation of $M_2(CO)_{10}$ in the presence of $Fe(CO)_5$, for example, yields species presumably having the structure indicated as XII.[166] Mixed M–M′ species can be either formed[115] or declusterified[170,171] by irradiation with ultraviolet light.

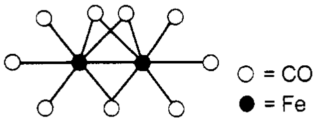
V. Iron, Ruthenium, and Osmium Carbonyls

A. Geometrical Structure

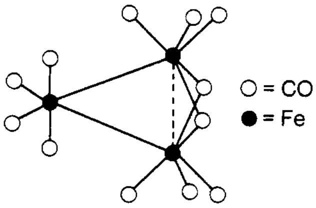
The commonly available carbonyls of iron include $Fe(CO)_5$ (XIII),[173] $Fe_2(CO)_9$ (XIV),[174,175] and $Fe_3(CO)_{12}$[176,177] (XV). In each case the central metal is formally in a zero oxidation state. The mononuclear and dinuclear complexes for Ru and Os are known but the most stable complexes containing only the metal and CO are $M_3(CO)_{12}$ having no bridging carbonyls as shown in XVI.[178-181]



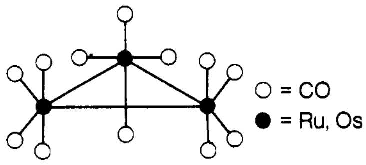
XIII



XIV

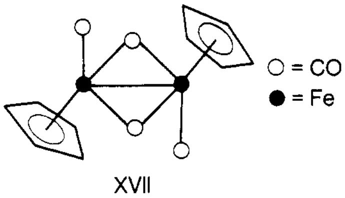


XV

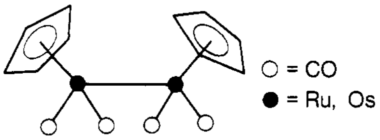


XVI

Cyclopentadienyl complexes containing Fe, Ru, Os, and CO are known and can exist as dimeric species with a metal-metal bond. Again, the first row Fe complex has bridging CO's (XVII)[182] while the second row Ru has both the bridged and nonbridged forms and the Os complex has no bridging CO's (XVIII).[182-185] These complexes may be viewed as having the central metal in a +1 oxidation state, but the complexes are diamagnetic by virtue of the direct M–M bond.



XVII



XVIII

Formally, the +2 oxidation state of the metals obtains in $M(CO)_4X_2$ (M = Fe, Ru, Os; X = Cl, Br, I), and the six ligands are in the usual O_h-like arrangement.[186] Higher oxidation states of iron apparently do not yield stable CO complexes and have been of little interest to photochemists.

B. Electronic Structure

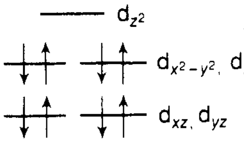
Even though the photochemistry of $Fe(CO)_5$ and its derivatives has been pursued vigorously for about 15 years, little effort has been devoted to a detailed study of electronic spectra. The spectrum of $Fe(CO)_5$ itself exhibits a shoulder in the vicinity of 40,000 cm^{-1} and another at 35,500 cm^{-1} but otherwise seems featureless.[25,187] Some uv–visible absorption data for Fe, Ru, and Os carbonyls are set out in Table XIX,[25,187-192] and in Table XX[193] the colors of the simple carbonyl complexes are given.

For the $M(CO)_nL_{5-n}$ complexes one might expect both CT and LF absorption. The d orbital ordering in D_{3h} symmetry is shown in Scheme VIII, and the first absorption maximum in $Fe(CO)_5$ has been identified as the

$$d_{xy}, d_{x^2-y^2} \rightarrow d_{z^2}$$

transition.[187] There seems to be only one other suggestion that the low-lying transitions in these complexes are LF.[194] Much of the intense high-energy absorption in $M(CO)_nL_{5-n}$ is logically associated with M→π*CO and M→L CT absorption.

SCHEME VIII



The information in Tables XIX and XX support the notion that some low-energy electronic transitions of the polynuclear compounds can be associated with the M–M bonds. There is also a tendency for the electronic transitions to be ordered energetically Os > Ru > Fe. Trivially, these data mean that the excited-state chemistry in the lighter metal complexes will likely occur at lower energy excitation wavelengths. Additionally, this observation may be correlated with greater thermal stability of the heavier metal complexes and perhaps greater relative enhanced lability upon electronic excitation. This final conclusion arises from *the assumption that depopulation or population of orbitals which are more stable or unstable, respectively, will have a more substantial effect on reactivity.*

C. Photoreactions

1. Substitution Reactions

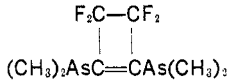
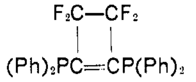
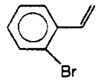
a. $M(CO)_nL_{5-n}$ Complexes

It now appears that all the $M(CO)_5$ (M = Fe, Ru, Os) complexes are photosensitive with respect to substitution of CO. Dissociative decay of $[M(CO)_5]^*$ to yield $M(CO)_4$ is almost a certainty with the coordinatively unsaturated $Fe(CO)_4$ having been observed by ir in low-temperature glassy media[51] and by flash photolysis.[195] The labeled CO's, ^{13}CO,[196a] $C^{18}O$,[196b] and ^{14}CO,[196c] have been incorporated into $Fe(CO)_5$ by photolysis. However, in the absence of any nucleophiles photoclusterification reactions proceed yielding $M_2(CO)_9$, $M_3(CO)_{12}$, and other species containing only M and CO. In fact, reaction 53[197] is the earliest reported photoreaction of a metal carbonyl.

$$2Fe(CO)_5 \xrightarrow{h\nu} Fe_2(CO)_9 + CO \qquad (53)$$

The formation of $Fe_3(CO)_{12}$ may be a thermal product of $Fe_2(CO)_9$ rather than a primary photoproduct *via* trimerization of three $Fe(CO)_4$ fragments. The earliest study[198] of $Ru(CO)_5$ and $Os(CO)_5$ in the absence of nucleophiles was carried out at ambient temperatures, and the corresponding $M_3(CO)_{12}$ species were obtained, but low-tem-

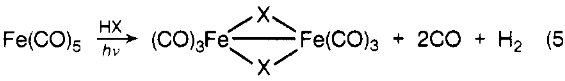
TABLE XXI. Photosubstitution of Mononuclear Iron, Ruthenium and Osmium Carbonyls

Starting complex	Entering group, L	Product(s)	Ref
$Fe(CO)_5$	CF_2CFCl	$Fe(CO)_4L$	200
$Fe(CO)_3[(MeO)_3P]_2$	Fluoro olefin	$Fe(CO)_2[(MeO)_3P]_2L$	201
$Ru(CO)_3[(MeO)_3P]_2$	Fluoro olefin	$Ru(CO)_2[(MeO)_3P]_2L$	201
$Ru(CO)_5$	PPh_3	$Ru(CO)_4L$	198
$Os(CO)_5$	PPh_3	$Os(CO)_4L$	198
$Fe(CO)_5$	 $(CH_3)_2As\overset{F_2C-CF_2}{C{=}C}As(CH_3)_2$	$Fe(CO)_4L$	202
$Fe(CO)_5$	 $(Ph)_2P\overset{F_2C-CF_2}{C{=}C}P(Ph)_2$	$Fe(CO)_3L$	202
(1,3-butadiene)- $Fe(CO)_3$	^{13}CO	(1,3-butadiene)- $Fe(CO)_n(L)_{3-n}$ ($n = 2, 1, 0$)	203
(1,3-butadiene)- $Fe(CO)_3$	PF_3	(1,3-butadiene)- $Fe(CO)L_2$	203
(1,3-cyclohexadiene)- $Fe(CO)_3$	PF_3	(1,3-cyclohexadiene)- $Fe(CO)_n(L)_{3-n}$ ($n = 2, 1, 0$)	204
$Fe(CO)_2(PF_3)_3$	PF_3	$Fe(PF_3)_5$	205
$Fe(CO)_5$		$Fe(CO)_4L$ $[Fe(CO)_3]_2L$	206
$Fe(CO)_5$	$AsPh_3$ PPh_3	$Fe(CO)_4L$ $Fe(CO)_3L_2$	207
$Fe(CO)_5$	Pyridine Piperidine Acetonitrile $CH_2{=}C{-}CN$	$Fe(CO)_4L$ (axial substitution)	208
$Fe(CO)_5$	CN^- SCN^-	$Fe(CO)_4L$	209

perature photolysis[199] yields the $M_2(CO)_9$ intermediates which undergo thermal reaction to give the trimeric species.

In the presence of a wide variety of entering groups $M(CO)_n(L)_{5-n}$ complexes are formed from $M(CO)_5$ (M = Fe, Ru, Os) and some recent examples are set out in Table XXI.[198,200-209] The examples cited clearly demonstrate the fact that CO lability in $M(CO)_nL_{5-n}$ and its derivatives is achieved upon photolysis. Further, the work of Clark and coworkers[203-205] provides the now familiar result that ligands most like CO will be incorporated to the highest degree. However, none of the studies reported thus far direct attention to the excited state substitution lability of ligands other than CO in the carbonyl derivatives.

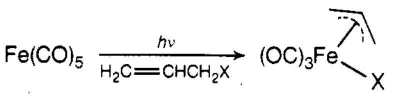
The coordinatively unsaturated intermediates formed *via* photolysis of $M(CO)_5$ are susceptible to oxidative addition, and some interesting reactions have been reported. For example, photolysis of $Fe(CO)_5$ in the presence of HX (X = Br, I) leads to the product indicated in reaction 54.[191] The reaction is thought to proceed by initial formation of $Fe(CO)_4(H)(X)$, followed by dimerization of this six-coordinate species to evolve CO and H_2. Reaction 55 represents another recent example where the primary product is stable.[81] Alkyl halides and allyl halides also add to the photogenerated coordinatively unsaturated species as in reaction 56.[210]



$$Fe(CO)_5 \xrightarrow[h\nu]{HX} (CO)_3Fe\overset{X}{\underset{X}{\rightleftharpoons}}Fe(CO)_3 + 2CO + H_2 \quad (54)$$

$$Fe(CO)_5 \xrightarrow[R_3Si-H]{h\nu} cis\text{-}Fe(CO)_4(SiR_3)(H) \quad (55)$$

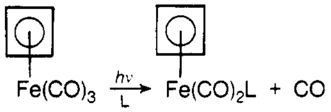
$$R = Ph,\ Cl$$



(56)

b. (arene)Fe(CO)$_n$(L)$_{3-n}$ Complexes

Both cyclobutadiene and cyclopentadienyl complexes of iron carbonyl have been subjected to photolysis and it appears, at least qualitatively, that loss of CO is the primary decay path of the excited state. The (cyclobutadiene)$Fe(CO)_3$ complex is very analogous to the (benzene)$Cr(CO)_3$ and (cyclopentadiene)$Mn(CO)_3$ in that each central metal is formally d^6. Thus, being like the Cr and Mn systems, it is not surprising that reaction 57 appears to dominate the chemical action. There are now several reports describing the formation of the substituted complexes.[211-214] Release of cyclobutadiene itself is probably a very inefficient primary excited state decay path of $(C_4H_4)Fe(CO)_3$.



(57)

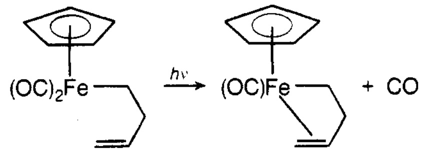
A larger number of simple photosubstitution reactions have been carried out with cyclopentadienyliron carbonyl complexes. Complexes of the formula $(Cp)Fe(CO)_2(X)$ (X = halogen, alkyl, etc.) have received considerable attention, and some recent photosubstitution products are collected in Table XXII.[82,85,135,215,216] As with prior examples, CO photosubstitution can be achieved by using good π-acceptor entering groups. It is even possible to displace the ligand X in certain cases though this does not appear to be an important primary photoprocess. Homolytic cleavage of the Fe–X bond might be expected

TABLE XXII. Photosubstitution Reactions of CpFe(CO)$_2$X

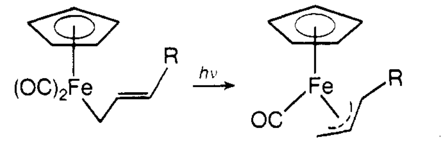
Starting material	Entering group, L	Product(s)	Ref
$(Cp)Fe(CO)_2I$	Et_2NPF_2	$(Cp)Fe(CO)LI$	82
		$(Cp)Fe(L)_2I$	
	$C_5H_{10}NPF_2$	$(Cp)Fe(L)_2I$	
	$[Ph_2PCH_2CH_2PPhCH_2]_2$	$[(Cp)FeL]^+I^-$	135
$(Cp)Fe(CO)_2Br$	$C_5H_{10}NPF_2$	$(Cp)Fe(L)_2I$	82
	$(Ph_2PCH_2CH_2)_2PPh$	$[(Cp)FeL]^+Br$	85
$(Cp)Fe(CO)_2Cl$	$Ph_2PCH_2CH_2PPh_2$	$(Cp)FeLCl$	85
	$(Ph_2PCH_2CH_2)_2PPh$	$[(Cp)FeL]^+Cl^-$	85
$(Cp)Fe(CO)_2Sn(CH_3)_3$	$SbPh_3$	$(Cp)Fe(CO)LSnPh_3$	215
		$(Cp)FeL_2SnPh_3$	
$(Cp)Fe(CO)_2SnPh_3$	$(CH_3)_2PPh$	$(Cp)FeL_2SnPh_3$	215
$[(Cp)Fe(CO)_2]_2$	$Ph_2PC{\equiv}CPPh_2$	$[(Cp)_2Fe_2(CO)_3]L$	216

upon higher photolysis to achieve a $\sigma \rightarrow \sigma^*$ excitation, while LF transitions may not labilize the halides since they are π-donor groups and would gain some stability *via depopulation* of the metal π-d level.

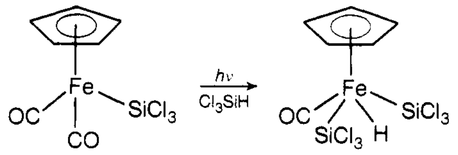
Other interesting consequences of CO dissociation from $(Cp)Fe(CO)_2X$ include intramolecular rearrangements as shown in reactions 58[217] and 59.[218] Additionally, it is known that the coordinatively unsaturated metal is susceptible to oxidative addition reaction 60.[81]



(58)



(59)



(60)

2. *Photoreactions of Polynuclear Iron, Ruthenium, and Osmium Carbonyls*

Excited-state reactions of polynuclear Fe, Ru, and Os carbonyls include both substitution and declusterification. Some recent low-temperature work with the $Fe_2(CO)_9$ reveals in this case that loss of CO occurs to yield $Fe_2(CO)_8$ upon photolysis[219] (reaction 61). When the

$$Fe_2(CO)_9 \xrightarrow[\text{Ar, 20°K}]{h\nu} Fe_2(CO)_8 + CO \qquad (61)$$

same reaction was carried out in a nitrogen matrix, evidence was obtained for the nitrogen complex $Fe_2(CO)_8N_2$. On the other hand, numerous mononuclear $Fe(CO)_nL_{5-n}$ complexes can be formed *via* the photolysis of $Fe_2(CO)_9$ in the presence of an entering group L. It is plausible that the mechanism of formation of the mononuclear species is first the generation of $Fe_2(CO)_8$ which scavenges L and subsequently decomposes, yielding $Fe(CO)_4L$ and a second $Fe(CO)_4$ which reacts with L. The bridging CO's in $Fe_2(CO)_9$ may preclude efficient cleavage of the Fe–Fe bond by $\sigma \rightarrow \sigma^*$ excitation of the metal–metal bond.

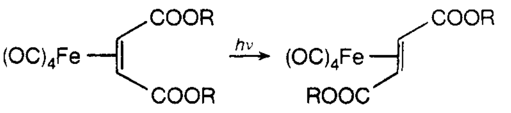
The $M_3(CO)_{12}$ (M = Fe, Ru, Os) have all received some attention, and a variety of confusing observations have been made. In Table XXIII,[220-224] we present a number of examples of photodeclusterification involving conversion of the trinuclear carbonyls to dinuclear and mononuclear species. However, the reports[225-227] of simple CO substitution upon photolysis of $M_3(CO)_{12}$ seem to preclude the conclusion that the exclusive excited-state decay path of $M_3(CO)_{12}$ is M–M bond cleavage. In view of the high reactivity expected for $Os(CO)_4$ and $Ru(CO)_4$, further work along these lines would be fruitful.

Dinuclear $[(Cp)Fe(CO)_2]_2$ has been shown to give both CO substitution[216] and mononuclear species upon photolysis.[228-230] More definitive information regarding the relative efficiency of M–M bond cleavage *vs.* CO substitution is likely to be obtained by study of $[(Cp)Os(CO)_2]_2$ where there are apparently no bridging CO groups. This system can be viewed as an electronic analog of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ where efficient M–M bond cleavage has been established (*vide supra*).

3. *Photoinitiated Reaction of Ligands*

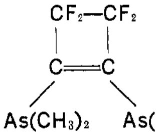
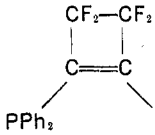
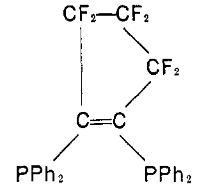
Reaction of ligands coordinated to Fe, Ru, and Os carbonyls and, in particular, Fe carbonyls, has been an area of active interest, and a number of reactions can be accelerated by, or are a unique result of, photolysis. Olefin reactions, including cis–trans isomerization, double bond migration, and oligomerization have been facilitated by irradiation of metal carbonyl species containing Fe, Ru, or Os. Additionally, several carbonylation reactions have been carried out by similar techniques. Examples of these and some mechanistic information are developed below.

Some of the photoassisted reactions of ligands using Fe, Ru, and Os carbonyls are set out in Table XXIV.[231-245] Simple olefin isomerization with $Fe(CO)_5$ has been known for some time and the role of the light in these reactions is probably to dissociate CO from the central metal to bind the olefin, since subsequent olefin rearrangements seem to parallel known thermal reactions. Thus, in this sense $Fe(CO)_5$, being the precursor to a thermally catalytic species, acts as a photocatalyst. In particular, attempts[246] to generate *cis*-stilbene from *trans*-stilbene (that is movement away from the thermodynamic ratio) have failed, in contrast to the results with $W(CO)_6$ and $Mo(CO)_6$ (*vide supra*). On the other hand, cis–trans isomerization of some olefins occurs only upon photolysis, and the olefin remains coordinated as in reaction 62.[237] In this case a maximum quantum efficiency of only 1.0 is possible. Reaction 62 exemplifies another point: cis–trans isomerization can occur without the pres-



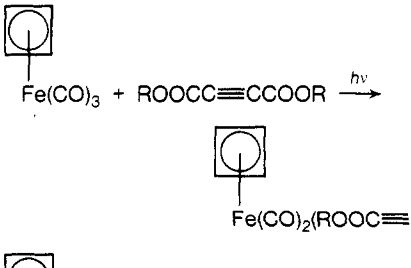
(62)

TABLE XXIII. Photodeclusterification of $M_3(CO)_{12}$ Complexes

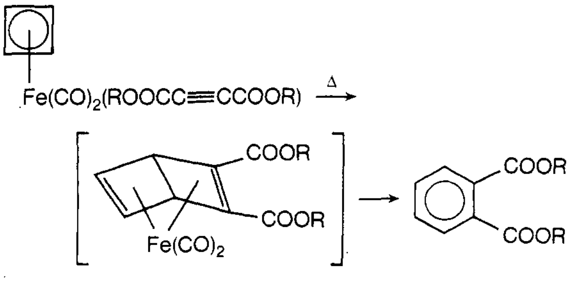
Starting carbonyl	Entering group	Product(s)	Ref
$Os_3(CO)_{12}$	$R_3Si—H$ $R = CH_3, C_2H_5$	$R_3SiOs(CO)_4H$ $(R_3Si)_2Os(CO)_4$ $[R_3SiOs(CO)_4]_2$ $(CH_3)_3SnOs(CO)_4H$ $(CH_3)_3GeOs(CO)_4H$	220–222
	1,5-Cyclooctadiene	(1,3-cycloocta-diene)$Os(CO)_3$ (1,5-cycloocta-diene)$Os(CO)_3$	223
	1,3-Cyclooctadiene	(1,3-cycloocta-diene)$Os(CO)_3$	
$Ru_3(CO)_{12}$	 ≡ ffars	$Ru_2(CO)_6$(ffars)	224
	 ≡ ffos	$Ru_2(CO)_6$(ffas) $Ru(CO)_3$(ffos)	
		$Ru_2(CO)_6(f_6fos)$ $Ru(CO)_3(f_6fos)$	
	$(CH_3)_3Si—H$ $(CH_3)_3Ge—H$ $Cl_3Ge—H$ $(CH_3)_5Si_2—H$	$[(CH_3)_3Si]_2Ru(CO)_4$ $[(CH_3)_2Ge)Ru(CO)_4]_2$ *cis*-$(Cl_3Ge)_2Ru(CO)_4$ $[(CH_3)_3SiRu(CO)_3$-μ-$Si(CH_3)_2]_2$	220–222

ence of allylic hydrogens ruling out a π-allyl hydride as the exclusive mechanism for olefin rearrangements. A σ-bonded olefin as in IX or CT excited states could account for this fact. For the hydrogen shift reactions, though, a metal hydride seems to be the most likely possibility and has been proposed as an intermediate in the thermal reactions.[247]

The olefin cycloaddition reactions provide some interesting examples of the utility of using the metal photoassistance technique. For example, the reactions of cyclobutadiene when coordinated to iron are carried out by the route indicated in reactions 63 and 64. The high efficiency for CO dissociation from the ("arene")$Fe(CO)_3$ probably precludes efficient direct release of cyclobutadiene and is, hence, held ready for reaction with the entering group. Coordinated trimethylenemethyl can also be held in a similar way to undergo reaction with entering olefins. The role of the light is again to make available a coordination site for the entering olefin.

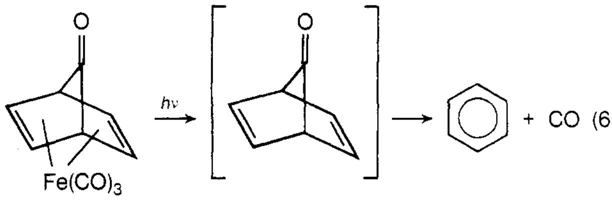


(63)



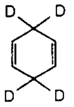
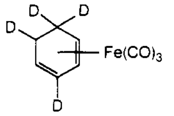
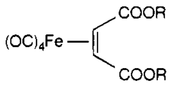
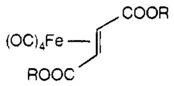
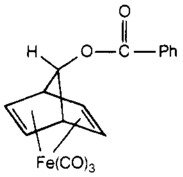
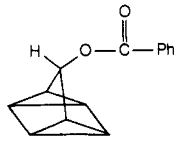
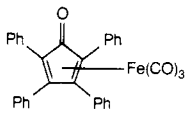
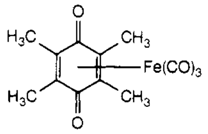
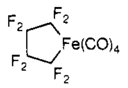
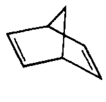
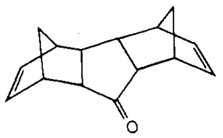
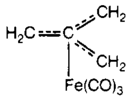
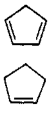
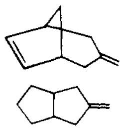
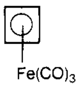
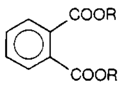
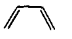
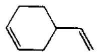
(64)

Though not encountered in the photochemistry of $M(CO)_6$ (M = Cr, Mo, W) and their olefin derivatives, many olefin reactions photoassisted by $Fe(CO)_5$ include carbonylation or decarbonylation of the ligand. One recent example (reaction 65)[248] is a simple example of decarbonylation, but the starting material provides another case where a reactive species is stabilized upon coordination. Incidently, in reaction 65 and in other situations where four- or six-electron donor olefins phenomenologically undergo photoinduced decomplexation, it is unlikely that such a process is an important *primary* excited-state decay path. Rather, it seems that CO dissociation occurs yielding a coordinatively unsaturated intermediate which can result in formal, if not literal, oxidation of the iron. Subsequent rapid thermal decomposition of the iron carbonyl-olefin complex gives uncomplexed olefin in the medium. Some other reactions which involve incorporation of CO into the final product are given in Table XXIV. The intermediate XIX[249] has been isolated from the reaction of $Fe(CO)_5$ and PhC≡CPh and may be a precursor to (tetraphenylcyclopentadienone)$Fe(CO)_3$. Inser-

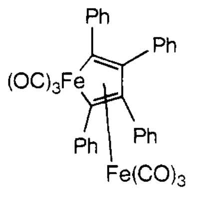


(65)

TABLE XXIV. Ligand Localized Reactions Initiated by Photolysis of Iron, Ruthenium, and Osmium Carbonyls

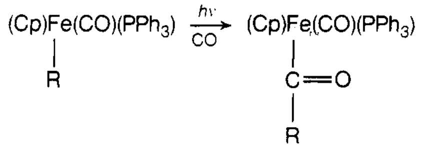
Initial metal carbonyl	Initial ligand	Product(s)	Ref
A. Olefin Isomerizations			
$Fe(CO)_5$			231, *cf.* also 232
	1-Alkenes	Internal alkenes	233–235
	$H_2C{=}CHCH_2OC_6H_5$ $H_2C{=}CHCH_2OC_2H_5$	$CH_3CH{=}CHOC_6H_5$ $CH_3CH{=}CHOC_2H_5$	236
			237
			238
$Os_3(CO)_{12}$	1,5-Cyclooctadiene	(1,3-cyclooctadiene)$Os(CO)_3$	223
B. Olefin Cyclo Addition Reactions			
$Fe(CO)_5$	$PhC{\equiv}CPh$		239
	$CH_3C{\equiv}CCH_3$		240
	CF_2CF_2		241
			242
			243
	$ROOCC{\equiv}CCOOR$		211, 244
$Fe(CO)_2(NO)_2$			245

tion[250,251] and elimination[252] of CO has been induced in alkyl and acyl iron carbonyl complexes, respectively, according to reactions 66 and 67. Reaction 67 probably proceeds *via* an initial photodissociation of a coordinated CO followed by an intramolecular rearrangement to yield the alkyl complex.

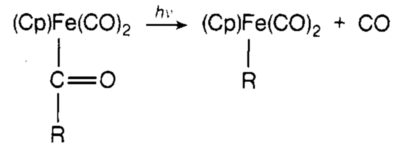


XIX

The hydrogenation of olefin iron tetracarbonyls and tricarbonyls has been achieved by the photolysis in the presence of acetic acid.[194] Olefins hydrogenated by this route include 1,3-dienes and alkenoates. Hydrogenation is thought to proceed *via* the scheme in reactions 68–71. This addition reaction cannot be catalytic since the iron carbonyl species is destroyed. The reaction efficiency was demonstrated to be wavelength dependent, probably reflecting the relative efficiencies of CO dissociation (eq

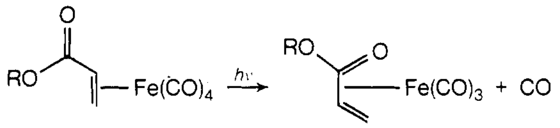


$$\underset{\substack{|\\R}}{(Cp)Fe(CO)(PPh_3)} \xrightarrow[CO]{h\nu} \underset{\substack{|\\C=O\\|\\R}}{(Cp)Fe(CO)(PPh_3)} \qquad (66)$$

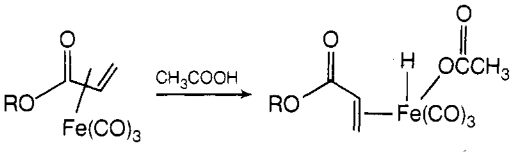


$$\underset{\substack{|\\C=O\\|\\R}}{(Cp)Fe(CO)_2} \xrightarrow{h\nu} \underset{\substack{|\\R}}{(Cp)Fe(CO)_2} + CO \qquad (67)$$

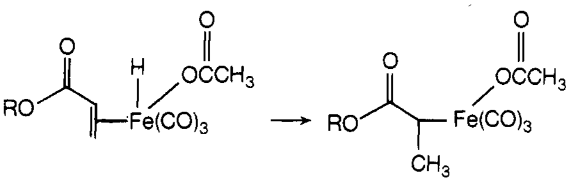
68) upon LF or M→olefin CT excitation, the former yielding a relatively large degree of olefin substitution.



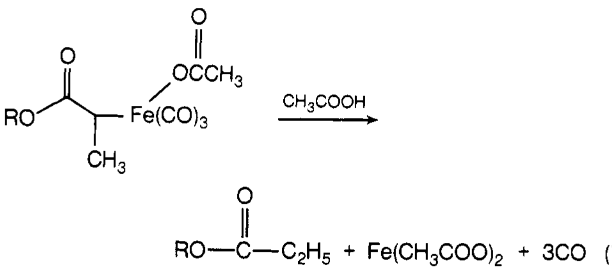
(68)



(69)

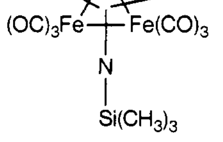


(70)

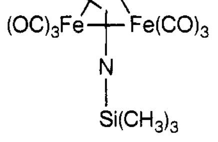


(71)

Fixation of molecular H_2 by Fe, Ru, and Os carbonyl complexes has been achieved by several workers and photo-assisted hydrogenation of olefins has been carried out under mild conditions. Iron pentacarbonyl itself has recently been shown to photoassist the hydrogenation of alkenes, 1,3-dienes, and alkynes at 20° and less than 10 psi of H_2.[253] The complexes $M(CO)_2(PPh_3)_2H_2$ (M = Fe, Ru, Os) have been prepared by 365-nm irradiation of the corresponding $M(CO)_3(PPh_3)_2$ complexes in the presence of H_2.[254] The dihydrido complex XX generated by photolysis of XXI can affect hydrogenation of methyl acrylate.[255] In all of these situations the primary photoprocess probably involves dissociation of CO to generate coordinative unsaturation.



XX



XXI

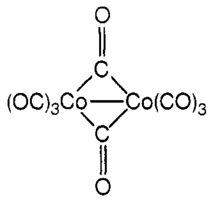
VI. Cobalt, Rhodium, and Iridium Carbonyl

A. Geometrical and Electronic Structures

TABLE XXV. Photosubstitution Reactions of Cobalt Carbonyls

Starting carbonyl	Entering group, L	Product(s)	Ref
$Co(CO)_3(NO)$	PPh_3	$Co(CO)_2(NO)L$	260
	PF_3	$Co(CO)_{3-n}(NO)(L)_n$ ($n = 1, 2, 3$)	261
	*CO	$Co(^*CO)_3(NO)$	74
$RCo(CO)_4$	PF_3	$RCo(CO)_{4-n}(L)_n$ ($n = 1, 2, 3, 4$)	262
$(Cp)Co(CO)_2$	Cyclooctatraene	(Cp)CoL	263
$Co_2(CO)_8$	1,3-Butadiene	$[Co(CO)_2L]_2$	264

Cobalt carbonyl containing only Co and CO is found as $Co_2(CO)_8$ having the structure in XXII by X-ray studies,[256] but in solution exists in equilibrium with XXIII.[257] The central metal is zerovalent and is formally d^9 but diamagnetic because of the Co–Co bond. A detailed electronic structure has not appeared, but one may expect both LF electronic transitions associated with a metal center having $\sim D_{3h}$ symmetry and a M–M transition. Interestingly the paramagnetic monomer $Co(CO)_4$ has been formed upon sublimation of $Co_2(CO)_8$ to a probe at −196°.[258] The situation as to whether the $Rh_2(CO)_8$ and $Ir_2(CO)_8$ exist is apparently uncertain. The $M_4(CO)_{12}$ (M = Co, Rh, Ir) and other polynuclear species have been characterized structurally but have received little or no attention from photochemists.



XXII

$(CO)_4Co—Co(CO)_4$

XXIII

The (π-C_5H_5)$M(CO)_2$ (M = Co, Rh, Ir) involve complexes of the d^8 configuration with the metal in a formal +1 oxidation state. The colors of the complexes are red, orange, and yellow for the Co, Rh, and Ir, respectively, consistent with the expected increase of LF splittings going down the group.

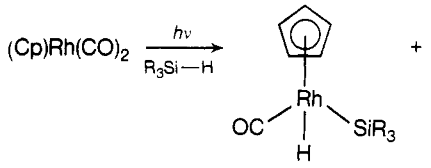
Finally, of interest here is the four-coordinate $Co(CO)_3NO$ complex which may be viewed as isoelectronic with $Ni(CO)_4$ having a d^{10} configuration. Electron diffraction studies[259] indicate a tetrahedral arrangement of the four ligands surrounding the central metal.

B. Photochemistry of Cobalt, Rhodium, and Iridium Carbonyls

The photochemistry of these metal complexes has not been developed to a great extent, but some familiar patterns are emerging. First, simple photosubstitution of CO is an important photoreaction and, at least for $CO_2(CO)_8$, some photoinduced M-M bond cleavage has been reported.

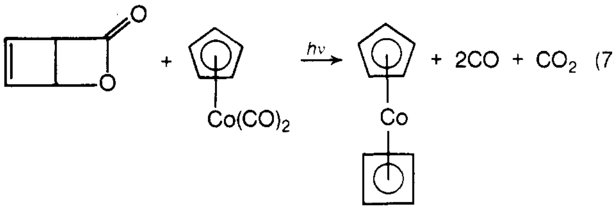
Examples of photosubstitution reactions of cobalt carbonyls are presented in Table XXV.[74,260-264] The entering groups in each case are all good π-acceptor ligands and with PF_3 all of the CO's can be replaced in either $Co(CO)_3NO$[261] or $RCo(CO)_4$.[262] The examples in Table XXV include systems of d^8, d^9, and d^{10} configuration. Though studies with the second and third row systems are not common, there are some results which suggest that similar photoprocesses obtain. The $(Cp)Rh(CO)_2$ complex apparently undergoes loss of CO upon photolysis giving reactions 72[265a] and 73.[265b] The oxidative addition to the coordinatively unsaturated intermediate should generally yield a fairly stable complex since the low-spin d^6 configuration will be achieved. An interesting example of this is

$$(Cp)Rh(CO)_2 \xrightarrow{h\nu} (Cp)_2Rh_2(CO)_3 + CO \qquad (72)$$



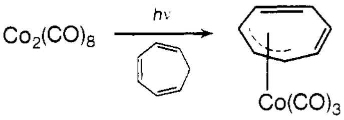
(73)

indicated in reaction 74 where the Co(I) changes to the substitution inert Co(III) state.[266]



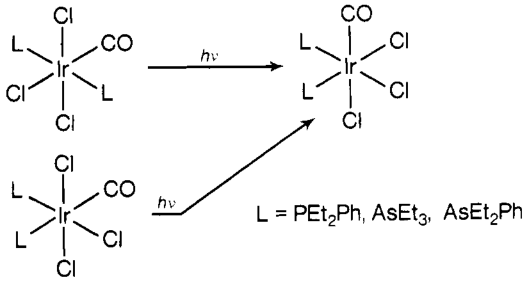
(74)

The cleavage of the M–M bond in $Co_2(CO)_8$ is exemplified by reaction 75,[267] but at this point it is not clear what the primary photoprocess involves.



(75)

We note, finally, with respect to the Co, Rh, and Ir group that the intramolecular isomerizations 76 occur apparently without decomposition.[268] This is curious because one would expect fairly efficient ligand substitution especially for CO which would be most affected by π-d → σ*-d excitation being a good π-acceptor ligand.



(76)

VII. Photochemistry of Nickel Carbonyls

Nickel carbonyl, $Ni(CO)_4$, has a d^{10} electronic configuration and is of tetrahedral geometry.[269] The absorption spectrum[30] is banded exhibiting shoulders at 42,270 and 44,500 cm^{-1} and a maximum at 48,550 cm^{-1} ($\epsilon \approx 10^5$). These transitions are associated with excitations of electrons in the t_2 and e levels of the metal to ligand localized orbitals.[30]

Photolysis of $Ni(CO)_4$ in the gas phase,[270] solution,[271] or the solid state[272] results in CO dissociation (reaction 77). The quantum yield of formation of CO is somewhat dependent on the excitation wavelength in *n*-hexane increasing from 0.22 at 366 nm to 0.50 near 240 nm. At 15°K the $Ni(CO)_3$ intermediate has C_{3v} symmetry from ir measurements.[272]

$$Ni(CO)_4 \xrightarrow{h\nu} Ni(CO)_3 + CO \qquad (77)$$

Elucidation of the photoprocesses in substituted nickel carbonyls has not been reported. However, photoassisted reaction of olefins have been carried out using derivatives of $Ni(CO)_4$.[273]

VIII. Summary

Many of the qualitative aspects of metal carbonyl photochemistry are known, and in particular a rather dramatic increase in lability in the M–CO bond seems virtually universal upon photoexcitation. Photolysis of the substituted derivatives of the binary compounds often results in alternate deactivation pathways at least as some fraction of the chemical action. Despite the collosal number of known metal carbonyls and their derivatives (many synthesized with light), there is a rather disappointing amount of sophistication regarding structure-reactivity relationships.

The reviewer feels that several areas merit focused attention. First, information concerning the nature of the electronic states available at optical energies should be pursued. Identification of the reactive excited states and their conversion pathways to other electronic states is of interest. Developing geometrical and electronic structure-reactivity relationships is of importance. And, finally, as chemists, our knowledge concerning primary processes in metal carbonyls should be directed toward generation of catalytically active species and synthetically useful molecules.

Acknowledgment. The research carried out in the reviewer's laboratory cited in the references was supported by the National Science Foundation.

IX. References and Notes

(1) A list of 30 review articles on metal carbonyls and their derivatives appears in E. W. Abel and F. G. A. Stone, *Quart. Rev., Chem. Soc.*, **24**, 498 (1970).
(2) E. Koerner von Gustorf and F.-W. Grevels, *Fortschr. Chem. Forsch.*, **13**, 366 (1969).
(3) W. Strohmeier, *Angew. Chem.*, **76**, 873 (1964).
(4) (a) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, New York, N. Y., 1970, Chapter 17; (b) "The Organic Chemistry of Iron," E. A. Koerner von Gustorf and F.-W. Grevels, Ed., Academic Press, New York, N. Y., in press.
(5) W. Strohmeier, *Fortschr. Chem. Forsch.*, **10**, 306 (1968).
(6) E. W. Abel and F. G. A. Stone, *Quart. Rev., Chem. Soc.*, **23**, 325 (1969).
(7) Structural determinations: (a) W. Rudorff and U. Hofmann, *Z. Phys. Chem.*, **B28**, 351 (1935); (b) L. O. Brockway, R. V. G. Ewens, and M. W. Lister, *Trans. Faraday Soc.*, **34**, 1350 (1938); (c) F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **84**, 4432 (1962).
(8) (a) W. Hieber, W. Beck, and G. Braun, *Angew. Chem.*, **72**, 795 (1960); (b) L. B. Handy, J. K. Ruff, and L. F. Dahl, *J. Amer. Chem. Soc.*, **92**, 7312 (1970).
(9) We adopt the formalism that cyclobutadiene dianion, cyclopentadiene anion, and benzene are six-electron donors and hence can occupy three coordination sites.
(10) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience, New York, N. Y., 1972, pp 968–969.
(11) N. A. Beach and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 5713 (1968).
(12) M. A. Graham, M. Poliakoff, and J. J. Turner, *J. Chem. Soc. A*, 2939 (1971).
(13) K. Mitteilung, *Z. Phys. Chem. (Frankfurt am Main)*, **27**, 439 (1961).
(14) P. S. Braterman and A. P. Walker, *Discuss. Faraday Soc.*, **47**, 121 (1969).
(15) D. J. Darensbourg and T. L. Brown, *Inorg. Chem.*, **7**, 959 (1968).
(16) M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Amer. Chem. Soc.*, **93**, 4336 (1971).
(17) M. Wrighton, G. S. Hammond, and H. B. Gray, *Inorg. Chem.*, **11**, 3122 (1972).
(18) M. Wrighton, Ph.D. Thesis, California Institute of Technology, 1972.
(19) M. Wrighton, unpublished results.
(20) M. Wrighton, G. S. Hammond, and H. B. Gray, *Mol. Photochem.*, **5**, 179 (1973).
(21) H. Saito, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jap.*, **41**, 359 (1968).
(22) H. Saito, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jap.*, **41**, 863 (1968).
(23) D. G. Carroll and S. P. McGlynn, *Inorg. Chem.*, **7**, 1285 (1968).
(24) M. Wrighton and J. Haverty, *Z. Naturforsch. B*, submitted for publication; and unpublished results.
(25) R. T. Lundquist and M. Cais, *J. Org. Chem.*, **27**, 1167 (1962).
(26) "Absorption Spectra in the UV and Visible Region," Vol. IX, L. Lang, Ed., Academic Press, New York, N. Y., 1967, pp 13–16.

(27) M. Y. Darensbourg and D. J. Darensbourg, *Inorg. Chem.*, **9**, 32 (1970).
(28) H. B. Gray and N. A. Beach, *J. Amer. Chem. Soc.*, **85**, 2922 (1963).
(29) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965, pp 57–60.
(30) A. F. Schreiner and T. L. Brown, *J. Amer. Chem. Soc.*, **90**, 3366 (1968).
(31) B. N. Figgis, "Introduction to Ligand Fields," Wiley, New York, N. Y., 1966, p 158.
(32) M. Wrighton, H. B. Gray, and G. S. Hammond, *Mol. Photochem.*, **5**, 165 (1973).
(33) (a) Reference 31, pp 234–237; (b) F. A. Cotton, "Chemical Applications of Group Theory," 2nd ed, Wiley, New York, N. Y., 1971, pp 260–263, 364.
(34) H. B. Gray, "Electrons and Chemical Bonding," W. A. Benjamin, New York, N. Y., 1965, p 199.
(35) (a) D. F. Gutterman and H. B. Gray, *J. Amer. Chem. Soc.*, **93**, 3364 (1971); (b) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965); (c) H.-H. Schmidtke, *Z. Phys. Chem. (Frankfurt am Main)*, **45**, 305 (1965); (d) H.-H. Schmidtke, *Inorg. Chem.*, **5**, 1682 (1966).
(36) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962, pp 106–107.
(37) "Organic Synthesis via Metal Carbonyls," Vol. 1, I. Wender and P. Pino, Ed., Wiley, New York, N. Y., 1968, p 173.
(38) Reference 37, p 159.
(39) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," New York, N. Y., 1966.
(40) W. Strohmeier and H. Hellmann, *Chem. Ber.*, **98**, 1598 (1965).
(41) R. J. Watts and G. A. Crosby, *J. Amer. Chem. Soc.*, **94**, 2606 (1972).
(42) J. N. Demas and G. A. Crosby, *J. Amer. Chem. Soc.*, **92**, 7262 (1970).
(43) A. I. Ryskin, A. M. Tkachuk, and N. A. Tolstoi, *Opt. Spectrosc. (USSR)*, **18**, 238 (1965).
(44) P. D. Fleischauer and P. Fleischauer, *Chem. Rev.*, **70**, 199 (1970).
(45) Reference 29, pp 24 and 48–50.
(46) G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, **37**, 1962 (1962).
(47) (a) M. O'Sullivan and A. C. Testa, *J. Amer. Chem. Soc.*, **92**, 5842 (1970); (b) *ibid.*, **92**, 258 (1970).
(48) K. K. Chatterjee and L. S. Forster, *Spectrochim. Acta*, **20**, 1603 (1964); **21**, 213 (1965).
(49) (a) M. Wrighton and D. L. Morse, submitted for publication; (b) Y. Kaizu, I. Fujita, and H. Kobayashi, *Z. Phys. Chem. (Frankfurt am Main)*, **79**, 298 (1972).
(50) A. G. Massey and L. E. Orgel, *Nature (London)*, **191**, 1387 (1961).
(51) (a) I. W. Stolz, G. R. Dobson, and R. K. Sheline, *J. Amer. Chem. Soc.*, **84**, 3589 (1962); (b) *ibid.*, **85**, 1013 (1963).
(52) W. Strohmeier and K. Gerlach, *Chem. Ber.*, **94**, 398 (1961).
(53) G. R. Dobson, *J. Phys. Chem.*, **69**, 677 (1965).
(54) J. Nasielski, P. Kirsch, and L. Wilputte-Steinert, *J. Organometal. Chem.*, **29**, 269 (1971).
(55) J. M. Kelly and A. Morris, *Rev. Latinoamer. Quim.*, **2**, 163 (1972).
(56) (a) J. M. Kelly, H. Hermann, and E. A. Koerner von Gustorf, IUPAC Symposium on Photochemistry, Baden-Baden, Germany, 1972, Paper No. 34, p 119 of the Manuscripts of Contributed Papers; (b) J. M. Kelly, H. Hermann, and E. G. Koerner von Gustorf, *Chem. Commun.*, 105 (1973).
(57) J. A. McIntyre, *J. Phys. Chem.*, **74**, 2403 (1970).
(58) A. Vogler, *Z. Naturforsch. B*, **25**, 1069 (1970).
(59) W. Strohmeier, D. von Hobe, G. Schonauer, and H. Laporte, *Z. Naturforsch.*, **17b**, 502 (1962).
(60) W. Strohmeier and D. von Hobe, *Chem. Ber.*, **94**, 2031 (1961).
(61) W. Strohmeier and D. Von Hobe, *Z. Phys. Chem. (Frankfurt am Main)*, **34**, 393 (1962).
(62) (a) D. J. Darensbourg, M. Y. Darensbourg, and R. J. Dennenberg, *J. Amer. Chem. Soc.*, **93**, 2807 (1971); (b) G. Schwenzer, M. Y. Darensbourg, and D. J. Darensbourg, *Inorg. Chem.*, **11**, 1967 (1972).
(63) R. Matheiu and R. Poilblanc, *Inorg. Chem.*, **11**, 1858 (1972).
(64) R. Matheiu, M. Lenzi, and R. Poilblanc, *Inorg. Chem.*, **9**, 2030 (1970).
(65) R. J. Clark and P. I. Hoberman, *Inorg. Chem.*, **4**, 1771 (1965).
(66) I. W. Stolz, G. R. Dobson, and R. K. Sheline, *Inorg. Chem.*, **2**, 1264 (1963).
(67) (a) W. Strohmeier and H. Hellmann, *Z. Naturforsch.*, **18b**, 769 (1963); (b) *Chem. Ber.*, **96**, 2859 (1963); (c) *ibid.*, **97**, 1877 (1964); (d) *ibid.*, **98**, 1598 (1965); (e) W. Strohmeier, G. Popp, and J. F. Guttenberger, *ibid.*, **99**, 165 (1966); (f) W. Strohmeier, J. F. Guttenberger, and F. J. Muller, *Z. Naturforsch.*, **22b**, 1091 (1967); (g) J. F. Guttenberger and W. Strohmeier, *Chem. Ber.*, **100**, 2807 (1967).
(68) W. Strohmeier and D. von Hobe, *Z. Naturforsch.*, **18b**, 981 (1963).
(69) A. N. Nesmeyanov, D. N. Kursanov, V. N. Setkina, V. D. Vil'chevaskaya, N. K. Baranetskaya, A. I. Krylova, and L. A. Gluskchenko, *Dokl. Akad. Nauk SSSR*, **199**, 1336 (1971).
(70) M. Herberhold and W. Golla, *J. Organometal. Chem.*, **26**, C27 (1971).
(71) B. V. Lokshin, V. I. Zdanovich, N. K. Baranetskaya, V. N. Setkina, and D. N. Kursanov, *J. Organometal. Chem.*, **37**, 331 (1972).
(72) R. J. Angelici and L. Busetto, *Inorg. Chem.*, **7**, 1935 (1968).
(73) E. O. Fischer and P. Kuzel, *Z. Naturforsch.*, **16b**, 475 (1961).
(74) W. Strohmeier and D. von Hobe, *Z. Naturforsch.*, **18b**, 770 (1963).
(75) W. Strohmeier and F.-J. Muller, *Chem. Ber.*, **102**, 3608 (1969).
(76) (a) H. Werner, K. Deckelmann, and U. Schonenberger, *Helv. Chim. Acta*, **53**, 2002 (1970); (b) F. A. Cotton and F. Zingales, *J. Amer. Chem. Soc.*, **83**, 351 (1961); (c) E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 2323 (1959).
(77) W. P. Anderson, W. G. Blenderman, and K. A. Drews, *J. Organometal. Chem.*, **42**, 139 (1972).
(78) G. Natta, R. Ercoli, F. Calderazzo, and E. Santambrozio, *Chim. Ind. (Milan)*, **40**, 1003 (1958).
(79) D. A. Brown, D. Cunningham, and W. K. Glass, *Chem. Commun.*, 306 (1966).
(80) D. A. Brown, W. K. Glass, and B. Kumar, *Chem. Commun.*, 736 (1967).
(81) W. Jetz and W. A. G. Graham, *Inorg. Chem.*, **10**, 4 (1971).
(82) R. B. King, W. C. Zipperer, and M. Ishaq, *Inorg. Chem.*, **11**, 1361 (1972).
(83) R. B. King, P. N. Kapoor, and R. N. Kapoor, *Inorg. Chem.*, **10**, 1841 (1971).
(84) R. J. Haines, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc. A*, 94 (1967).
(85) R. B. King, L. W. Houk, and K. H. Pannell, *Inorg. Chem.*, **8**, 1042 (1969).
(86) R. B. King and K. H. Pannell, *Inorg. Chem.*, **7**, 2356 (1968).
(87) K. W. Barnett, and P. M. Treichel, *Inorg. Chem.*, **6**, 294 (1967).
(88) R. B. King and R. N. Kapoor, *Inorg. Chem.*, **8**, 2535 (1969).
(89) (a) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **4**, 486 (1965); (b) R. B. King and A. Fronzaglia, *J. Amer. Chem. Soc.*, **88**, 709 (1966).
(90) M. L. H. Green and A. N. Stear, *J. Organometal. Chem.*, **1**, 230 (1964).
(91) R. J. Haines, R. S. Nyholm, and M. G. B. Stiddard, *J. Chem. Soc. A*, 43 (1968).
(92) M. Wrighton and D. S. Ginley, unpublished results; *cf.*, however, A. R. Burkett, T. J. Meyer, and D. G. Whitten, *J. Organometal. Chem.*, **67**, 67 (1974).
(93) A. T. McPhail, G. R. Knox, C. G. Robertson, and G. A. Sim, *J. Chem. Soc. A*, 205 (1971).
(94) M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Amer. Chem. Soc.*, **92**, 6068 (1970).
(95) M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Amer. Chem. Soc.*, **93**, 3285 (1971).
(96) M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Organometal. Chem.*, **70**, 283 (1974).
(97) J. Nasielski, P. Kirsch, and L. Wilputte-Steinert, *J. Organometal. Chem.*, **27**, C13 (1971).
(98) M. Wrighton and M. A. Schroeder, *J. Amer. Chem. Soc.*, **95**, 5764 (1973), and unpublished results.
(99) W. Jennings and B. Hill, *J. Amer. Chem. Soc.*, **92**, 3199 (1970).
(100) S. Sato, *Pure Appl. Chem.*, **16**, 87 (1968).
(101) R. E. Kellogg and W. T. Simpson, *J. Amer. Chem. Soc.*, **87**, 4230 (1965).
(102) F. D. Tsay, H. B. Gray, and J. Danon, *J. Chem. Phys.*, **54**, 3760 (1971).
(103) (a) W. P. Griffith and G. Wilkinson, *J. Chem. Soc.*, 1629 (1959); (b) M. E. Kimball, J. P. Martella, and W. C. Kaska, *Inorg. Chem.*, **6**, 414 (1967); (c) J. Halpern, *Accounts Chem. Res.*, **3**, 386 (1970).
(104) (a) M. Cais, E. N. Frankel, and A. Rejoan, *Tetrahedron Lett.*, 1919 (1968); (b) E. N. Frankel, E. Selke, and C. A. Glass, *J. Amer. Chem. Soc.*, **90**, 2446 (1968).
(105) J. E. Ellis, Ph.D. Thesis, Massachusetts Institute of Technology, 1971.
(106) W. Beck and R. E. Nitzschmann, *Z. Naturforsch.*, **17b**, 577 (1962).
(107) B. N. Figgis, "Introduction to Ligand Fields," Interscience Publishers, New York, N. Y., 1966, pp 245–247.
(108) (a) P. S. Braterman and A. Fullarton, *J. Organometal. Chem.*, **31**, C27 (1971); (b) A. Davison and J. E. Ellis, *ibid.*, **31**, 239 (1971).
(109) (a) A. N. Nesmeyanov, *Advan. Organometal. Chem.*, **10**, 56 (1972); (b) E. O. Fischer, E. Louis, and R. J. J. Schneider, *Angew. Chem., Int. Ed. Engl.*, **7**, 136 (1968); (c) E. O. Fischer and R. J. J. Schneider, *Angew. Chem.*, **79**, 537 (1967); (d) R. Tsumura and N. Hagihara, *Bull. Chem. Soc. Jap.*, **38**, 1901 (1965).
(110) (a) L. F. Dahl and R. E. Rundle, *Acta Crystallogr.*, **16**, 419 (1963); (b) M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, **4**, 1140 (1965); (c) L. F. Dahl, E. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, **26**, 1750 (1957).
(111) L. F. Dahl and C. H. Wei, *Acta Crystallogr.*, **16**, 611 (1963).
(112) A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and I. S. Kolomnikov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 194 (1963).
(113) T. Kruck and M. Hofler, *Angew. Chem.*, **76**, 786 (1964).
(114) G. O. Evans, J. P. Hargaden, and R. K. Sheline, *Chem. Commun.* 186 (1967).
(115) G. O. Evans and R. K. Sheline, *J. Inorg. Nucl. Chem.*, **30**, 2862 (1968).
(116) P. A. Agron, R. D. Ellison, and H. A. Levy, *Acta Crystallogr.*, **23**, 1079 (1967).
(117) (a) G. B. Blakney and W. F. Allen, *Inorg. Chem.*, **10**, 2763 (1971); (b) C. H. Bamford, J. W. Burley, and M. Coldbeck, *J. Chem. Soc., Dalton Trans.*, 1846 (1972).
(118) H. B. Gray, E. Billig, A. Wojcicki, and M. Farona, *Can. J. Chem.*, **41**, 1281 (1963).
(119) D. Ottesen, M. Wrighton, and H. B. Gray, unpublished results.
(120) M. Wrighton and D. L. Morse, *J. Amer. Chem. Soc.*, **96**, 998 (1974), and unpublished results.
(121) R. A. Levenson, H. B. Gray, and G. P. Ceasar, *J. Amer. Chem.*

Soc., **92**, 3653 (1970).
(122) R. A. Levenson, Ph.D. Thesis, Columbia University, 1970.
(123) D. P. Keeton and F. Basolo, *Inorg. Chim. Acta*, **6**, 33 (1972).
(124) (a) M. Wrighton and D. Bredesen, *J. Organometal. Chem.*, **50**, C35 (1973); (b) K. Moedritzer, *Syn. Inorg. Metal. Org. Chem.*, **1**, 63 (1971).
(125) M. Wrighton and D. Bredesen, unpublished results.
(126) A. J. Rest and J. J. Turner, *Chem. Commun.*, 375 (1969).
(127) A. Berry and T. L. Brown, *Inorg. Chem.*, **11**, 1165 (1972).
(128) J. F. Ogilvie, *Chem. Commun.*, 323 (1970).
(129) M. L. H. Green and P. L. I. Nagy, *Advan. Organometal. Chem.*, **2**, 327 (1964).
(130) T. H. Whitesides and R. A. Budnick, *Chem. Commun.*, 1514 (1971).
(131) W. J. Miles, Jr., and R. J. Clark, *Inorg. Chem.*, **7**, 1801 (1968).
(132) A. S. Foust, J. K. Hoyano, and W. A. G. Grahm, *J. Organometal. Chem.*, **32**, C65 (1971).
(133) (a) W. Strohmeier, C. Barbeau, and D. von Hobe, *Chem. Ber.*, **96**, 3254 (1963); (b) W. Strohmeier and D. von Hobe, *Z. Phys. Chem. (Frankfurt am Main)*, **34**, 393 (1962).
(134) J. K. Ruff, *Inorg. Chem.*, **10**, 409 (1971).
(135) R. B. King, R. N. Kapoor, M. S. Saran, and P. N. Kapoor, *Inorg. Chem.*, **10**, 1851 (1971).
(136) W. Strohmeier and K. Gerlach, *Z. Naturforsch.*, **15b**, 675 (1960).
(137) W. Strohmeier, J. F. Guttenberger, and H. Hellmann, *Z. Naturforsch.*, **19b**, 353 (1964).
(138) W. Strohmeier and J. F. Guttenberger, *Chem. Ber.*, **97**, 1871 (1964).
(139) W. Strohmeier and C. Barbeau, *Z. Naturforsch.*, **17b**, 848 (1962).
(140) M. L. Ziegler and R. K. Sheline, *Inorg. Chem.*, **4**, 1230 (1965).
(141) R. J. Angelici and W. Loewen, *Inorg. Chem.*, **6**, 682 (1967).
(142) E. O. Fischer and M. Herberhold, *Experimentia, Suppl.*, **9**, 259 (1964).
(143) R. S. Nyholm, S. S. Sandhu, and M. H. B. Stiddard, *J. Chem. Soc.*, 5916 (1963).
(144) W. Strohmeier and J. F. Guttenberger, *Chem. Ber.*, **96**, 2112 (1963).
(145) R. B. King and M. S. Saran, *Inorg. Chem.*, **10**, 1861 (1971).
(146) E. O. Fischer and M. Herberhold, *Z. Naturforsch.*, **16b**, 841 (1961).
(147) W. Strohmeier and J. F. Guttenberger, *Z. Naturforsch.*, **18b**, 80 (1963).
(148) P. M. Treichel, E. Pitcher, R. B. King, and F. G. A. Stone, *J. Amer. Chem. Soc.*, **83**, 2593 (1961).
(149) A. J. Rest, *Chem. Commun.*, 345 (1970).
(150) J. B. Wilford, P. M. Treichel, and F. G. A. Stone, *Proc. Chem. Soc.*, 218 (1963).
(151) A. J. Oliver and W. A. G. Graham, *Inorg. Chem.*, **9**, 2578 (1970).
(152) H. C. Clark, J. D. Cotton, and J. H. Tsai, *Inorg. Chem.*, **5**, 1582 (1966).
(153) H. C. Clark and J. H. Tsai, *Inorg. Chem.*, **5**, 1407 (1966).
(154) J. B. Wilford, P. M. Treichel, and F. G. A. Stone, *J. Organometal. Chem.*, **2**, 119 (1964).
(155) A. G. Osborne and M. H. B. Stiddard, *J. Chem. Soc.*, 634 (1964).
(156) J. R. Miller and D. H. Myers, *Inorg. Chim. Acta*, **5**, 215 (1970).
(157) J. Lewis, R. S. Nyholm, A. G. Osborne, S. S. Sandhu, and M. H. B. Stiddard, *Chem. Ind. (London)*, 1398 (1963).
(158) C. Barbeau, *Can. J. Chem.*, **45**, 161 (1967).
(159) R. J. Clark, J. P. Hargaden, H. Haas, and R. K. Sheline, *Inorg. Chem.*, **7**, 673 (1968).
(160) J. T. Moelwyn-Hughes, A. W. Garner, and N. Gordon, *J. Organometal. Chem.*, **26**, 373 (1971).
(161) G. Bor, *Chem. Commun.*, 641 (1969).
(162) M. L. Ziegler, H. Haas, and R. K. Sheline, *Chem. Ber.*, **98**, 2454 (1965).
(163) J. P. Crow, W. R. Cullen, and F. L. Hou, *Inorg. Chem.*, **11**, 2125 (1972).
(164) J. P. Crow, W. R. Cullem, F. L. Hou, L. Y. Y. Chan, and F. W. B. Einstein, *Chem. Commun.*, 1229 (1971).
(165) W. Hieber and W. Schrop, Jr., *Z. Naturforsch.*, **15b**, 271 (1960).
(166) M. W. Lindauer, G. O. Evans, and R. K. Sheline, *Inorg. Chem.*, **7**, 1249 (1968).
(167) J. C. Kwok, Ph.D. Thesis, University of Liverpool, 1971.
(168) C. H. Bamford and J. Paprotny, *Chem. Commun.*, 140 (1971).
(169) M. Wrighton and D. S. Ginley, unpublished results.
(170) T. Kruck, M. Hofler, and M. Noacke, *Chem. Ber.*, **99**, 1153 (1966).
(171) T. Kruck and M. Hofler, *Angew. Chem.*, **76**, 786 (1964).
(172) C. H. Bamford, P. A. Crowe, J. Hobbs, and R. P. Wayne, *Proc. Roy. Soc., Ser. A*, **292**, 153 (1966).
(173) (a) A. W. Hanson, *Acta Crystallogr.*, **15**, 930 (1962); (b) J. Donohue and A. Caron, *ibid.*, **17**, 663 (1964).
(174) (a) R. Brill, *Z. Kristallogr.*, **65**, 85 (1927); (b) H. M. Powell and R. V. G. Ewen, *J. Chem. Soc.*, 286 (1939).
(175) R. K. Sheline and K. S. Pitzer, *J. Amer. Chem. Soc.*, **72**, 1107 (1950).
(176) C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, **88**, 1821 (1966); **91**, 1351 (1969).
(177) (a) K. Noack, *Helv. Chim. Acta*, 45, 1847 (1962); (b) F. A. Cotton and G. Wilkinson, *J. Amer. Chem. Soc.*, **79**, 752 (1957).
(178) E. R. Corey and L. F. Dahl, *Inorg. Chem.*, **1**, 521 (1962).
(179) E. R. Corey and L. F. Dahl, *J. Amer. Chem. Soc.*, **83**, 2203 (1961).
(180) D. K. Huggin, N. Flitcroft, and H. D. Kaesz, *Inorg. Chem.*, **4**, 166 (1965).
(181) D. L. Smith, *J. Chem. Phys.*, **42**, 1460 (1965).
(182) O. S. Mills, *Acta Crystallogr.*, **11**, 620 (1958).
(183) R. D. Fischer, A. Vogler, and K. Noack, *J. Organometal. Chem.*, **7**, 135 (1967).
(184) F. A. Cotton and G. Yagupsky, *Inorg. Chem.*, **6**, 15 (1967).
(185) A. R. Manning, *J. Chem. Soc. A*, 1319 (1968).
(186) L. F. Dahl and D. L. Wampler, *Acta Crystallogr.*, **15**, 946 (1962).
(187) M. Dartiguenave, Y. Dartiquenave, and H. B. Gray, *Bull. Soc. Chim. Fr.*, **12**, 4223 (1969).
(188) W. Hieber and H. Beutner, *Z. Naturforsch.*, **17b**, 211 (1962).
(189) E. Koerner von Gustorf, O. Jaenicke, and O. E. Polansky, *Z. Naturforsch.*, **27b**, 575 (1972).
(190) E. Koerner von Gustorf, F.-W. Grevels, C. Kruger, G. Olbrich, F. Mark, D. Schulz, and R. Wagner, *Z. Naturforsch.*, **27b**, 392 (1972).
(191) E. Koerner von Gustorf, J. C. Hogan, and R. Wagner, *Z. Naturforsch.*, **27b**, 140 (1972).
(192) G. N. Schrauzer and G. Kratel, *J. Organometal. Chem.*, **2**, 336 (1964).
(193) (a) I. Wender and P. Pino, Ed., "Organic Synthesis via Metal Carbonyls," Vol. 1, Interscience Publishers, New York, N. Y., 1968, p. 39; (b) E. W. Abel and F. G. A. Stone, *Quart Rev., Chem. Soc.*, **23**, 325 (1969).
(194) E. A. Koerner von Gustorf, F.-W. Grevels, M. K. Das, O. Jaenicke, and R. Knoesel, Manuscript No. 36, IUPAC Symposium on Photochemistry, Baden-Baden, Germany, 1972.
(195) E. Koerner von Gustorf and M. E. Langmuir, unpublished results cited in ref 2.
(196) (a) G. Bor, *Inorg. Chim. Acta*, **3**, 191 (1969); (b) K. Noack and M. Ruch, *J. Organometal. Chem.*, **17**, 309 (1969); (c) D. F. Keely and R. E. Johnson, *J. Inorg. Nucl. Chem.*, **11**, 33 (1959).
(197) J. Dewar and H. O. Jones, *Proc. Roy. Soc., Ser. A*, **76**, 558 (1905).
(198) F. L'Eplattenier and F. Calderazzo, *Inorg. Chem.*, **6**, 1220 (1967).
(199) J. R. Moss and W. A. G. Graham, *Chem. Commun.*, 835 (1970).
(200) R. Fields, M. M. Germain, R. N. Haszeldine, and P. W. Wiggens, *J. Chem. Soc. A*, 1964, 1969 (1970).
(201) R. Burt, M. Cooke, and M. Green, *J. Chem. Soc. A*, 2975, 2981 (1970).
(202) W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *Inorg. Chem.*, **8**, 1464 (1969).
(203) J. D. Warren and R. J. Clark, *Inorg. Chem.*, **9**, 373 (1970).
(204) J. D. Warren, M. A. Busch, and R. J. Clark, *Inorg. Chem.*, **11**, 452 (1972).
(205) R. J. Clark, *Inorg. Chem.*, **3**, 1395 (1964).
(206) R. Victor, R. Ben-Shoshan, and S. Sarel, *Chem. Commun.*, 1241 (1971).
(207) J. Lewis, R. S. Nyholm, S. S. Sandhu, and M. H. B. Stiddard, *J. Chem. Soc.*, 2825 (1964).
(208) E. H. Schubert and R. K. Sheline, *Inorg. Chem.*, **5**, 1071 (1966).
(209) J. K. Ruff, *Inorg. Chem.*, **8**, 86 (1969).
(210) R. F. Heck and C. R. Boss, *J. Amer. Chem. Soc.*, **86**, 2580 (1964).
(211) (a) P. Reeves, J. Henery, and R. Pettit, *J. Amer. Chem. Soc.*, **91**, 5888 (1969); (b) J. S. Ward and R. Pettit, *ibid.*, **93**, 262 (1971).
(212) (a) A. Bond and M. Green, *Chem. Commun.*, 12 (1971); (b) A. Bond and M. Green, *J. Chem. Soc., Dalton Trans.*, 763 (1972).
(213) J. Font, S. C. Barton, and O. P. Strausz, *J. Chem. Soc., Dalton Trans.*, 499 (1970).
(214) F. M. Chaudhari and P. L. Pauson, *J. Organometal. Chem.*, **5**, 73 (1966).
(215) W. R. Cullen, J. R. Sams, and J. A. J. Thompson, *Inorg. Chem.*, **10**, 843 (1971).
(216) A. J. Carty, A. Efraty, T. W. Ng, and T. Birchall, *Inorg. Chem.*, **9**, 1263 (1970).
(217) M. L. H. Green and M. J. Smith, *J. Chem. Soc. A*, 3220 (1971).
(218) M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 189 (1963).
(219) M. Poliakoff and J. J. Turner, *J. Chem. Soc. A*, 2403 (1971).
(220) S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc. A*, 3147 (1970); 2559 (1969).
(221) A. Brockes, S. A. R. Knox, and F. G. A. Stone, *J. Chem. Soc. A*, 3469 (1971).
(222) S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc. A*, 2874 (1971).
(223) F. A. Cotton, A. J. Deeming, P. L. Josty, S. S. Ullah, A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J. Amer. Chem. Soc.*, **93**, 4624 (1971).
(224) W. R. Cullen and D. A. Harbourne, *Inorg. Chem.*, **9**, 1839 (1970).
(225) W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *Inorg. Chem.*, **9**, 702 (1970).
(226) P. J. Roberts and J. Trotter, *J. Chem. Soc. A*, 1479 (1971).
(227) W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *J. Amer. Chem. Soc.*, **90**, 3293 (1968).
(228) A. N. Nesmeyanov, L. G. Makarova, and V. N. Vinogradova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984 (1971).
(229) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **4**, 482 (1965).
(230) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **6**, 469 (1967).
(231) H. Alper, P. C. LePort, and S. Wolfe, *J. Amer. Chem. Soc.*, **91**, 7553 (1969).
(232) A. J. Birch, P. E. Cross, J. Lewis, D. A. White, and S. B. Wild, *J. Chem. Soc. A*, 332 (1968).
(233) F. Y. Asinger, B. Fell, and K. Schrage, *Chem. Ber.*, **98**, 381 (1965).
(234) F. Asinger, B. Fell, and G. Collin, *Chem. Ber.*, **96**, 716 (1963).
(235) M. D. Carr, V. V. Kane, and M. C. Whiting, *Proc. Chem. Soc., London*, 408 (1964).
(236) P. W. Jolly, F. G. S. Stone, and K. Mackenzie, *J. Chem. Soc.*,

6416 (1965).

(237) G. O. Schenck, E. Koerner von Gustorf, and M.-J. Jun, *Tetrahedron Lett.*, 1059 (1962).

(238) D. F. Hunt, C. P. Lillya, and M. D. Rausch, *J. Amer. Chem. Soc.*, **90**, 2561 (1968).

(239) (a) R. Markby, H. W. Sternberg, and I. Wender, *Chem. Ind. (London)*, 1381 (1959); (b) G. N. Schrauzer, *J. Amer. Chem. Soc.*, **81**, 5307 (1959).

(240) H. W. Sternberg, R. Markby, and I. Wender, *J. Amer. Chem. Soc.*, **80**, 1009 (1958).

(241) R. Fields, M. M. Germain, R. N. Haszeldine, and P. W. Wiggans, *Chem. Commun.*, 243 (1967).

(242) (a) R. Pettit, *J. Amer. Chem. Soc.*, **81**, 1266 (1959); (b) M. Green and E. A. C. Lucken, *Helv. Chim. Acta*, **45**, 1870 (1962).

(243) A. C. Day and J. T. Powell, *Chem. Commun.*, 1241 (1968).

(244) W. J. R. Tyerman, M. Kato, P. Kebarle, S. Masamune, O. P. Strausz, and H. E. Gunning, *Chem. Commun.*, 497 (1967).

(245) Unpublished results cited in ref 2.

(246) M. Wrighton and A. Cisar, unpublished results.

(247) T. A. Manuel, *J. Org. Chem.*, **27**, 3941 (1962).

(248) J. M. Landesberg and J. Sieczkowski, *J. Amer. Chem. Soc.*, **91**, 2120 (1969).

(249) W. Hubel and E. H. Braye, *J. Inorg. Nucl. Chem.*, **10**, 250 (1959).

(250) A. N. Nesmeyanov, I. V. Polovyanyuk, and L. G. Makarova, *J. Organometal. Chem.*, **7**, 329 (1967).

(251) P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *Inorg. Chem.*, **5**, 1177 (1966).

(252) R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **2**, 15 (1964).

(253) M. Wrighton and M. A. Schroeder, submitted for publication.

(254) D. Valentine, J. Valentine, and B. Sarver in "Photoexcited States," J. N. Pitts, Ed., Gordon and Breach, New York, N. Y., 1970.

(255) E. Koerner von Gustorf, I. Fischler, F.-W. Grevels, D. Schulz, and R. Wagner, Sixth International Conference on Organometallic Chemistry, Amherst, Mass., 1973, Abstract No. 46.

(256) G. G. Sumner, H. P. Klug, and L. E. Alexander, *Acta Crystallogr.*, **17**, 732 (1964).

(257) (a) K. Noack, *Spectrochim. Acta*, **19**, 1925 (1963); (b) G. Bor, *Spectrochim. Acta*, **19**, 2065 (1963).

(258) H. J. Keller and H. Wawersik, *Z. Naturforsch.*, **20b**, 938 (1965).

(259) L. O. Brockway and J. S. Anderson, *Trans. Faraday Soc.*, **33**, 1233 (1937).

(260) I. H. Sabherwal and A. Burg, *Chem. Commun.*, 853 (1969).

(261) R. J. Clark, *Inorg. Chem.*, **6**, 299 (1967).

(262) C. A. Udovich and R. J. Clark, *Inorg. Chem.*, **8**, 938 (1969).

(263) A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Jap.*, **33**, 425 (1960).

(264) E. O. Fischer, P. Kuzel, and H. P. Fritz, *Z. Naturforsch.*, **16b**, 138 (1961).

(265) (a) E. O. Fischer and K. Bittler, *Z. Naturforsch.*, **16b**, 835 (1961); (b) A. J. Oliver and W. A. G. Graham, *Inorg. Chem.*, **10**, 1 (1971).

(266) M. Rosenblum, B. North, D. Wells, and W. P. Giering, *J. Amer. Chem. Soc.*, **94**, 1239 (1972).

(267) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 785 (1964).

(268) P. R. Brookes, C. Masters, and B. L. Shaw, *J. Chem. Soc. A*, 3756 (1971).

(269) J. Ladell, B. Post, and I. Fankuchen, *Acta Crystallogr.*, **5**, 795 (1952).

(270) A. B. Callear, *Proc. Roy. Soc., Ser. A*, **265**, 71 (1961).

(271) A. P. Garratt and H. W. Thompson, *J. Chem. Soc.*, 1817 (1934).

(272) A. J. Rest and J. J. Turner, *Chem. Commun.*, 1026 (1969).

(273) B. Hill, K. Math, D. Pillsbury, G. Voecks, and W. Jennings, *Mol. Photochem.*, **5**, 195 (1973).