ASPECTS OF ORGANO-TRANSITION-METAL PHOTOCHEMISTRY AND THEIR BIOLOGICAL IMPLICATIONS

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I. Introduction

Two questions may demonstrate why the authors of this survey found it rather complicated to give a concise definition of its scope: What is

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photochemistry? and What is organometallic chemistry? The answers we would like to suggest reflect our personal point of view.

Photochemistry is the study of chemical changes brought about by light. It encompasses all processes "participating in the formation and deactivation of electronically excited molecules" (*454*). Some of its aspects may be considered as photophysics, some as photobiology; however, any arbitrary demarcation would not be in accord with the interdisciplinary character of this field.

We consider *organometallic chemistry* to be the chemistry of compounds in which metals are bound to groups or molecules that are under the regime of organic chemistry. We do not make any distinction whether bonding occurs via carbon or another element, as for instance N, P, O, or S. In many transformations of organic material involving metals, the site of bonding and the primary reactive steps remain obscure anyhow.

Organometallic compounds are often made from "inorganic" starting materials, are applied in organic syntheses, and play a significant role in biochemistry. Too narrow a definition could only harm the possibilities of interdisciplinary cross-fertilization. Our view deviates somewhat from general practice. In a narrow sense, organometallic compounds should contain a direct carbon-to-metal bond. According to a recent IUPAC ruling, a differentiation is even made with respect to the nature of this bond. Whereas a σ-bonded metal alkyl is named an "organometallic compound," a π-alkylmetal compound is named a "coordination compound" (*273*).

After these programmatic remarks, it is obvious that a survey on organometallic photochemistry can only cover specifically selected areas of this broad field.

In this article we have tried to stress mechanistic and preparative aspects. We hope to address the inorganic and organometallic chemist who is interested in photochemistry as a method to be applied to his problems. The following points have, therefore, been emphasized: methods for the photochemical production and characterization of unstable and short-lived intermediates (discussed in a section on primary processes in organometallic photochemistry); important reaction principles; photosyntheses of new organometallic compounds (especially at low temperatures); photochemical transformations of organic compounds using metals as templates; mechanistic investigations using photochemical methods for the synthesis of, and the search for, postulated intermediates in organometallic reactions occurring in the dark; and application of organometallic photoreactions as models for biochemical studies.

The discussion is restricted to the photochemistry of organo-transition-metal compounds in low-oxidation states. It basically deals with the photochemistry of metal carbonyls and derivatives and metal compounds containing σ- and π-bonded organic systems. Sandwich compounds, such as ferrocene (*68*), have been omitted and will be discussed elsewhere (*55*).

Because an extensive survey of this field was published in 1969 from our laboratory (*332*), the coverage of literature in this present article is based on a search of *Chemical Abstracts* from 1969 to the middle of 1974. The volume of literature has been growing rapidly, and much of the information about photochemical work in organometallic chemistry is hidden and often hard to find. We, therefore, did not attempt a complete coverage of all work done in the field. We also felt unable to incorporate all the available information into one article of limited size. According to the plan of emphasizing preparative and mechanistic aspects, we have tried to present Sections III, D and IV as completely as possible. A more detailed discussion of the primary photoprocesses will be given elsewhere (*55*). The remarks on biological applications (Section V) are supposed to whet the reader's appetite rather than to give an extensive survey.†

We draw the reader's attention to two excellent books (*1a*, *27*), some recent reviews on the photochemistry of coordination compounds (*533*, *388*, *386*, *26*, *590*), and two valuable surveys of metal carbonyl photochemistry (*584*, *609*). Comprehensive annual reports on inorganic and organometallic photochemistry are found in the *Specialist Periodical Reports* (*433*). Finally, an annual highlights section on this subject is featured by *Molecular Photochemistry* (*202*).

II. Principles of Photochemistry

Quinkert (*454*) remarked that the chemistry of electronically excited states provides a new dimension in chemistry. This comment was founded on the different chemical reactivities of electronic ground and excited states. A photochemist must not only be concerned with the chemical consequences of photolysis but also with the ways in which the excited-state molecule can change its electronic state. Some of these processes are summarized briefly in Fig. 1 to familiarize the reader with the vocabulary of photochemistry (*434*). For a more detailed discussion the reader is referred to some of the excellent books in this field (*568*, *107*, *27*, *359*, *143*, *131*, *534*, *597*).

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† Much information on this subject is found in the numerous papers by R. J. P. Williams.

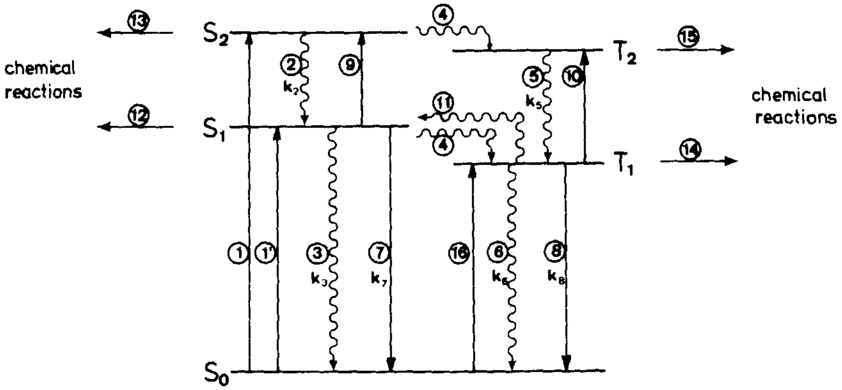

FIG. 1. Energy levels of excited states and transitions between them. Vertical straight lines represent radiative transitions; wavy lines nonradiative transitions. S = singlet, T = triplet, numbers are explained in text.

The state of a molecule produced on electronic excitation depends on the energy of the light quantum absorbed.† The excited states can dissipate their energy in different ways. Upper electronic states will usually be converted very fast to the lowest-excited states (process 2 in Fig. 1), from which further processes originate. The radiationless transition between states of the same multiplicity (e.g., processes 2, 3, and 5) is called internal conversion and that between states of different multiplicity (process 4), intersystem crossing. The radiative decay of excited states is termed fluorescence if it occurs between states of the same multiplicity (process 7) and phosphorescence if a change of multiplicity is involved (process 8). Emission after thermal back-population of S_1 from T_1 (process 11 followed by process 7) is called delayed fluorescence.

The probability of an electronic transition is controlled by symmetry, overlap, and spin requirements. The oscillator strengths of transitions are reduced by the following factors relative to a fully allowed transition: (a) about 10^{-5} if spin-forbidden (e.g., $S_0 \rightarrow T_1$); (b) 10^{-2} if overlap-forbidden (e.g., n-π^* transition of second-row heteroatoms); and (c) 10^{-1}–10^{-4} if symmetry or orbitally forbidden (e.g., parity or Laporte rule). The strictness of the spin rule is reduced by spin-orbit coupling, which plays an important role with the heavier elements. In some organometallic compounds, singlet–triplet absorptions (process 16 in Fig. 1) have been identified, but they are mostly

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† Only light absorbed can bring about a photochemical change, and usually each quantum absorbed activates only one molecule in the primary state.

restricted to compounds of third-row transition metals [e.g., $Mo(CO)_5$-$(NHEt_2)$, no singlet–triplet absorption; $W(CO)_5(NHEt_2)$, ${}^1A_1 \rightarrow {}^3E$ at 438 nm, $\varepsilon = 730$) (*609*, *619*, *620*)].

Chemical reactions (processes 12–15 in Fig. 1) can arise from any excited state, but most photoconversions originate from the lowest-excited states (S_1, T_1), since they have a longer lifetime than the upper states. This difference can be attributed to the larger energy gap between the ground state and first excited state. In reactions of organometallic compounds, reactions from upper-excited states are observed quite frequently (see Section IV).

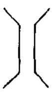
III. Primary Processes in Organometallic Photochemistry

This section is devoted to the methods used for studying primary photochemical processes (the production and decay of electronically excited states) (*359*) and their application to organometallic compounds. The following topics will be discussed: electronic absorption spectroscopy (UV/vis), luminescence, flash photolysis, photolysis in rigid media, and quenching and sensitization processes.

A. ELECTRONIC ABSORPTION SPECTROSCOPY

An indication of the number of excited states of a molecule accessible by direct absorption can often be derived from the absorption spectra (e.g., processes 1, 1′, and 16 in Fig. 1). The resolution of the spectra is of critical importance and can be increased by (a) measuring the spectra in the gas phase, (b) by measuring at low temperatures in a matrix or single crystal, (c) by using solvents of different polarity or hydrogen-bonding ability, (d) by using magnetic circular dichroism (*541*), or (e) by using circular dichroism if the compounds are optically active (*252*, 392) [possibly by introduction of ligands containing optically active groups (*335*)]. The assignment of the absorption bands is a major problem often requiring detailed theoretical treatment of the system under investigation.

The important kinds of electronic transitions in an organometallic compound can be described schematically using the simplified case of an olefin–transition metal complex. According to the Chatt-Duncanson picture (*111*), bonding in such a system can be described as being composed of two major components.

An oversimplified MO scheme can be derived from such a picture (Fig. 2) by considering the frontier orbitals of the metal and olefin (e.g., for the hypothetical Fe···  ; Fig. 3). Some of the resulting MO's

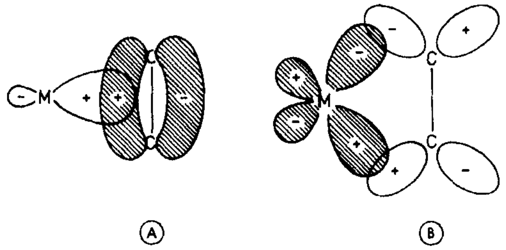


FIG. 2. Bonding between a metal and an olefin. (A) σ Donor bond, olefin → metal by overlap of an occupied olefin π-orbital with an unoccupied metal σ-orbital. (B) π-Backbonding, metal → olefin, by overlap of the unoccupied olefin π^*-orbital with an occupied metal d_π-orbital.

will have major contributions from the metal orbitals ($\pi_{1'}$, σ_2), others from the ligand orbitals (σ_1, π_2). Three important types of transitions may then occur.

i. *d-d Transitions*. These involve transitions between two orbitals of predominantly metal *d* character (transition A in Fig. 3). The result of such an excitation is a redistribution of electron density at the metal atom without any major change of charge. In the case of transition A in Fig. 3, the depopulation of a π-bonding orbital is accompanied by the population of the antibonding orbital σ_2. Such

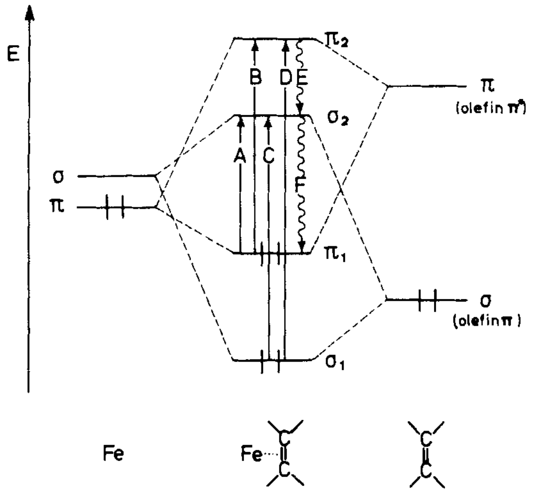


FIG. 3. Simplified MO scheme of an iron olefin species. Transitions A–F explained in text.

transitions often cause the dissociation of metal–ligand (M—L) bonds. This reaction is one of the most important phenomena in this branch of photochemistry.

ii. *Charge-transfer transitions.* In processes B and C, electronic transitions occur from orbitals of mainly metallic to orbitals of mainly ligand character or vice versa. Thus, transition B results in a charge-transfer from metal to ligands (CTML transition), whereas transition C causes a movement of charge in the opposite direction (CTLM transition). Either nucleophilic or electrophilic attack at the metal should be facilitated in the CT-excited states according to the direction of charge flow. Although *d-d* transitions are usually weak, the large transition moment of CT processes often results in strong absorption bands (for *d-d* processes $\varepsilon \simeq 1$–150 for spin-allowed transitions in octahedral complexes, $\varepsilon \simeq 1000$ for noncentrosymmetric complexes; for CT processes $\varepsilon \simeq 10^4$).

iii. *Intraligand transitions.* The third kind of transition relates to processes involving orbitals of mainly ligand character (e.g. transition D in Fig. 3.) It may also be possible to observe intraligand transitions of groups that are not involved in bonding to the metal. The frequencies of such transitions are often not influenced by coordination to the metal. In such cases they can be used to study the effects of the neighboring metal on the lifetime of the excited states and to check for intramolecular energy transfer, etc. (*604*, *618*, *615*, *627*, *628*).

A clear distinction among these different kinds of transitions is seldom possible in organometallic compounds. Although the excited states usually have mixed character, these approximations are still useful. The differences between the reactivity of the different types of excited states will be discussed in Section IV. However, most chemical reactions can be ascribed to the decay of *d-d* excited states.

Much work has recently been devoted to the development of theoretical models of excited state properties (*615*, *629*, *630*, *631*). There have also been attempts to draw conclusions about the nature of the excited states from the observed chemical reactivity (*236*, *615*).

Dependence of the photobehavior on the wavelength of irradiation is much more common among organometallic compounds than among organic compounds, for which the number of cases known is limited. It appears that fast chemical reactions can compete with internal conversion of excited states. As a result, small changes in the ligands often have a dramatic effect on the ratio of the corresponding rate constants.

Most of the available absorption data on metal carbonyl compounds have recently been reviewed in an excellent survey by Wrighton (*609*).

We have therefore restricted ourselves to the discussion of some examples from organoiron chemistry that illustrate the general points outlined above.

The UV spectra of $Fe(CO)_5$ shown in Fig. 4 demonstrate the effect of low-temperature measurements on the quality of the spectrum. Two major absorption bands can be observed at 77°K at 35,450 cm^{-1} ($\varepsilon = 3{,}900$) and at 41,670 cm^{-1} ($\varepsilon = 15{,}700$). The spectrum has been assigned (Table I) on the basis of detailed MO calculations (Fig. 5) (*147*).

Although the longest-wavelength transition occurs between two orbitals with predominantly *d* character, it gains intensity by mixing with ligand orbitals. The higher-energy absorption at ~41,500 cm^{-1} is assigned to a superposition of transitions to two orbitals with 77 and 99% π^* (CO) character, respectively.

The situation is even more complicated in the substituted carbonyls derived from $Fe(CO)_5$. Table II lists the UV spectra of a variety of olefin–tetracarbonyliron complexes (*236*).

The example of the fumaric acid–tetracarbonyliron complex (Fig. 6) demonstrates that circular dichroism (CD) spectra reveal more bands and are better resolved than the corresponding "normal" absorption spectra (*392*). Instead of using the tedious procedure of optical resolution, CD spectra of metal complexes can also be obtained by the introduction of optically active ligands. For instance, di-*l*-menthyl fumarate tetracarbonyliron shows extrema at [kK($\Delta\varepsilon$)] 27.8(−1.7), 32.9(+11.1),

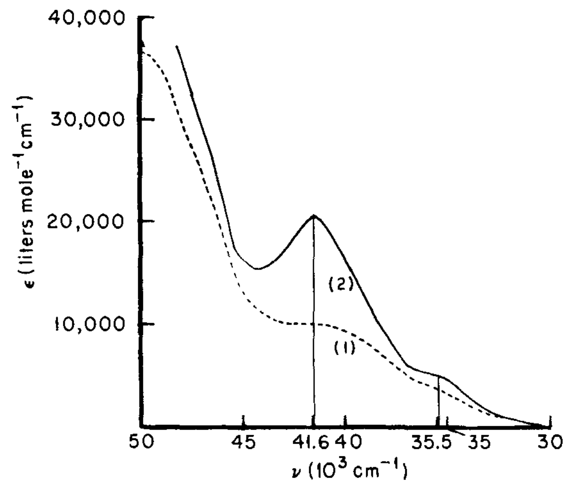


FIG. 4. Ultraviolet spectrum of $Fe(CO)_5$ in isopentane methylcyclohexane at 300°K (1) and at 77°K (2). [From Dartiguenave *et al.* (*147*).]

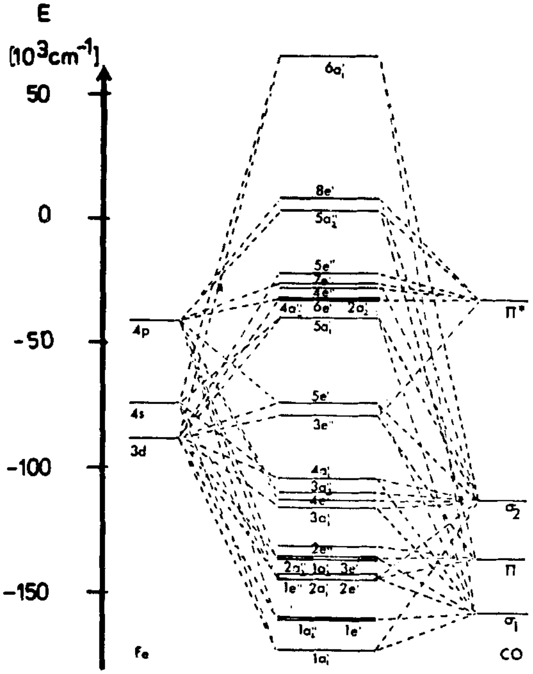


FIG. 5. Molecular orbital scheme of $Fe(CO)_5$. [From Dartiguenave *et al.* (*147*).]

TABLE I
ASSIGNMENT OF TRANSITIONS IN $Fe(CO)_5$[a]

Absorptions observed in cm^{-1} (ε in liters $mole^{-1}$ cm^{-1}) 300°K	Absorptions observed in cm^{-1} (ε in liters $mole^{-1}$ cm^{-1}) 77°K	Assignment	Calculated absorptions (cm^{-1})
35,500 (3,800)	35,450 (3,900)	$5e' \rightarrow 5a_1'$ allowed	34,000
		$3e'' \rightarrow 5a_1'$ forbidden	39,200
41,500 (10,200)	41,670 (15,700)	$5e' \rightarrow 6e'$ allowed	41,300
		$5e' \rightarrow 2a_2'$ allowed	41,400
		$5e' \rightarrow 4a_2''$ forbidden	41,000
50,000 (37,000)	—	$5e' \rightarrow 4e''$ allowed	45,800
		$3e'' \rightarrow 6e'$ allowed	46,500
		$3e'' \rightarrow 4a_2''$ allowed	46,200
		$3e'' \rightarrow 2a_2'$ forbidden	46,600
		$5e' \rightarrow 7e'$ allowed	48,500
		$3e'' \rightarrow 4e''$ allowed	51,000
		$5e' \rightarrow 5e''$ allowed	52,600
		$3e'' \rightarrow 7e'$ allowed	53,700

[a] Data from Dartiguenave *et al.* (*147*).

TABLE II

ULTRAVIOLET DATA OF SOME TETRACARBONYL–OLEFINIRON COMPLEXES IN *n*-HEXANE[a]

L in L—Fe(CO)$_4$	cm^{-1} × 10^{-3} (kK)[b]			
cis-1,2-Dibromoethylene	∼28.5 (WS) (470)	36 (S) (5,400)	∼43 (WS) (14,600)	46[c] (17,000)
trans-1,2-Dibromoethylene	∼28 (WS) (490)	34.7 (M) (5,680)	∼40.5 (WS) (10,200)	∼46 (17,000)
cis-1-Bromo-2-fluoroethylene[d]	∼29.5 (WS) (700)	∼37 (WS) (5,100)	—	—
trans-1-Bromo-2-fluoroethylene	∼29 (WS) (420)	∼36.5 (WS) (4,500)	∼40.5 (WS) (8,500)	46 (17,500)
cis-1,2-Dichloroethylene	∼29 (WS) (550)	37 (S) (4,900)	—	∼46 (18,300)
trans-1,2-Dichloroethylene	∼29 (WS) (290)	36.5 (S) (4,550)	∼43 (WS) (15,000)	46 (17,500)
Dimethylmaleate	∼29 (WS) (630)	38.5 (S) (7,700)	—	46 (20,400)
Dimethylfumarate	∼28.5 (WS) (710)	36.0 (M) (9,100)	—	46 (21,600)
Methylacrylate	∼29 (WS) (700)	38.5 (S) (7,600)	—	46 (20,000)
Ethylene tetracarboxylic acid–tetramethylester	∼30 (WS) (1,080)	37.3 (M) (9,430)	—	47 (19,000)
CO[e]	—	35.5 (3,800)	41.5 (10,200)	50 (37,000)

[a] From Grevels and Koerner von Gustorf (*236*).

[b] (WS) weak shoulder; (S) shoulder; (M) maximum.

[c] Measurement limit, possibly a shoulder or a maximum.

[d] Spectrum measured up to 41,000 cm^{-1}.

[e] From Dartiguenave *et al.* (*147*).

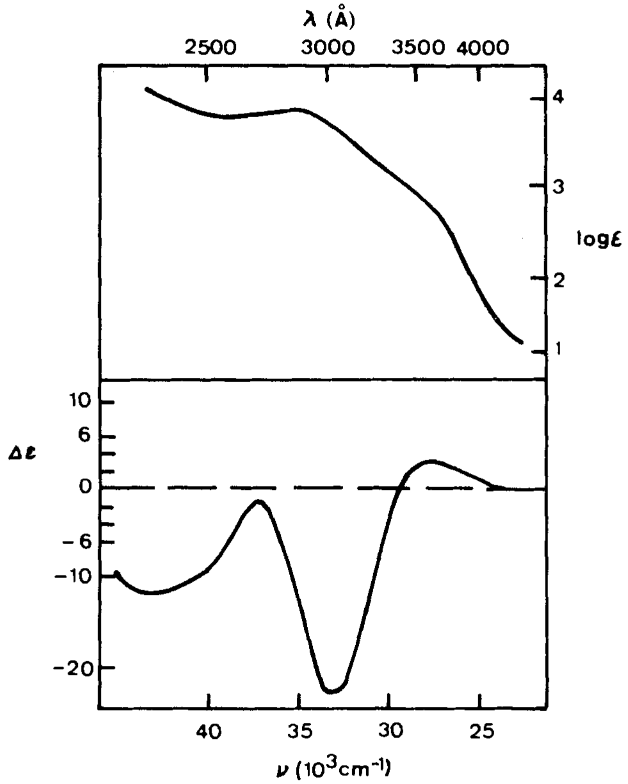
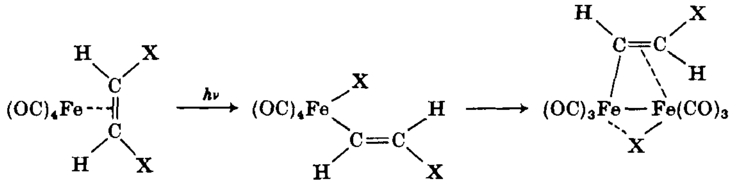


FIG. 6. Electronic and circular dichroism spectra of (−)-fumaric acid $Fe(CO)_4$ in methanol. [From Musco *et al.* (*392*).]

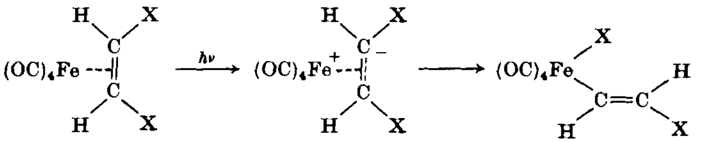
40(+ 4.5)(shoulder), 43.8(+ 6.2) (*335*). These positions compare quite well with those of fumaric acid–tetracarbonyliron shown in Fig. 6. The sign and size of $\Delta\varepsilon$ indicates a considerable enrichment of the *S*,*S*-dimentyl fumarate–iron tetracarbonyl complex.

Since the low symmetry (C_{2v}) of these complexes allows extensive mixing of Fe, CO, and olefin orbitals, the resulting MO's are of rather complex composition [for a detailed discussion, see Grevels and Koerner von Gustorf (*236*)]. It is not surprising, therefore, that photolysis results in the loss of both CO and olefin. However, the ratio of these two processes is wavelength-dependent (*93*).

The complexity of attempts to correlate observed photoreactions with the nature of the corresponding excited state is demonstrated by the study of the photoreactivity of η-(1,2-dihaloethylene)–tetracarbonyliron complexes (*236*). Irradiation in the 34–37,000 cm^{-1} region, led to (*3*).



(1) (2) (3) (1)

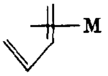


(1) (2) (2)

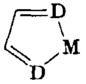
Compound **2** was detected by IR spectroscopy and transforms into **3** as the final product. Although compound **2** might be expected to originate from a CTML state, as shown in Eq. (2), a detailed study revealed that the primary process is the loss of CO, which is followed by oxidative addition of a C—X bond and readdition of CO. The reactive state was, therefore, assigned to a *d-d* excited state (leading to cleavage of a M—CO bond). Whether this reactive state is reached by direct excitation or by internal conversion remains an open question.

In Table III we have compiled a selection of absorption data for diene–metal complexes, the dienes being butadiene, substituted butadienes, and aza and oxa derivatives.

A comparison shows that absorption is observed in the same range ($\tilde{\nu}$ > 23,000 cm^{-1}) so long as the diene system functions as a 4π-electron donor system (**4**). Diazabutadiene complexes that are differently bonded (**5**) show a dramatically different spectrum with a strong transition in the 20,000 cm^{-1} area (*165*). This band shows remarkable solvent dependence indicating considerable CT character.



(4)



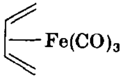
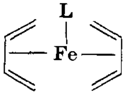
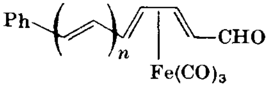
(5)

(D = heteroatom)

The absorption data given for **9** and **16** (Table III) are examples of transitions between ligand orbitals (*74*) that are little perturbed by the metal.

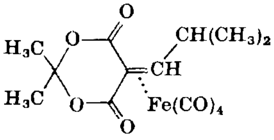
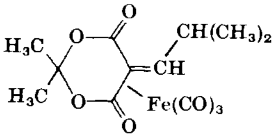
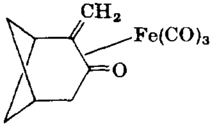
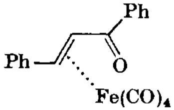
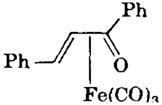
The assignment of the transitions in diene–tricarbonyliron complexes is difficult. The CD spectra of *trans,trans*-2,4-hexadienoic acid

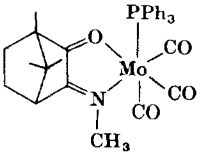
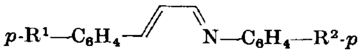
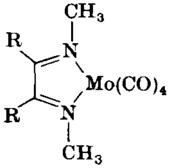
TABLE III
Absorption Data for Diene–Metal Carbonyls

Complex	Absorptions[a] $\tilde{\nu}$ in kK (ε in liters mole^{-1} cm^{-1})	Solvent	Ref.
 (6)	36 (2,500) (S at RT)	*n*-Hexane	*275*
	(M at LT)	Methylcyclohexane–isopentane	
	36 (S) (700)	Gas phase	
	49 (13,200)		
			
(7) L = CO	24.7 (180)	*n*-Hexane	*92*
	32 (S) (950)		
	36.5 (S) (2,400)		
	45 (20,000)		
(8) L = PF_3	25.2 (180)	Cyclohexane	*92*
	34 (S) (1,000)		
	38 (S) (2,300)		
	45 (17,000)		
			
(9) *n* = 0	37.9 (22,700)	Dichloromethane	*75*
n = 1	35 (22,300)		
n = 2	32 (24,500)		
n = 3	29.9 (23,000)		

(*continued*)

TABLE III (*Continued*)

Complex	Absorptions[a] $\tilde{\nu}$ in kK (ε in liters mole^{-1} cm^{-1})	Solvent	Ref.
 **(10)**	29.0 (S) (1,600) 41.0 (S) (12,000)	Cyclohexane	*338*
 **(11)**	24.0 (S) (520) 30.7 (2,400)	*n*-Hexane	*338*
 **(12)**	23.5 (S) (550) 29.7 (1,980) 42.2 (11,900)	Diethyl ether	*333*
 **(13)**	29.5 (S) (5,500) 32.5 (S) (8,600) 38.8 (22,400)	*n*-Hexane	*333*
	29.0 (S) (4,400) 33.2 (S) (13,200) 40.0 (22,800)	*n*-Hexane	*333*

 **(15)**	15.1^b		Acetone	*465*
	14.9^b		Benzene	*465*
				
(16) R^1 R^2			Cyclohexane	*74*
H H	35.6 (21,700)	32.8 (17,200)		
Cl Cl	35 (25,300)	32.6 (S) (22,100)		
OMe H	35 (20,900)	32.6 (S) (20,500)		
				
(17) R^1 R^2			Cyclohexane	*74*
H H	33.8 (26,700)	30.3 (S) (14,200)		
Cl Cl	32.9 (29,900)	29.8 (S) (20,300)		
OMe H	32.2 (S) (23,200)	30.9 (24,200)		
		29.4 (S) (21,100)		
	20^b		Dimethylformamide	*165*
	18.7^b		Benzene	
(18) R = H	21.7^b		Dimethylformamide	
R = CH_3	19.8^b		Benzene	

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[a] (S) shoulder; (M) maximum, (RT) room temperature, (LT) low temperature (89°K).

[b] Longest-wavelength absorption.

iron tricarbonyl reveal at least five different transitions in the 25–45 kK area (*392*).

According to SCCC calculations comprising charge and configuration iteration of the metal as well as of the ligand atoms, we can expect ten transitions in the 24,000–50,000 cm^{-1} area for **6**, and thirteen transitions in this region for **7** (*537*, *599*). These calculations also show that the MO's of photochemical interest have varying contributions from the diene, CO, and metal orbitals. However, for some of the electronically excited states, preferential cleavage of the Fe—CO or the Fe—diene bond is predicted in agreement with the experimental observations (see Section IV).

Valuable information about electronic spectroscopy of inorganic and main group organometallic compounds is found in Refs. *368* and *457*.

B. LUMINESCENCE

Luminescence appears to be a scarce phenomenon among organometallic compounds and can often only be studied in compounds isolated in glasses at temperatures of 77°K or below. Emission from complexes of the Group VIB metals (Cr, Mo, W) has received most attention. Although emission has been observed for most of the tungsten complexes studied, it is much less common among the lighter members of the group.

Luminescence has been reported for the following groups of metal carbonyl derivatives: (i) $W(CO)_5L$ (L = NR_3, NHR_2, NH_2R, pyridine, ROH, ROR, ketones) (*618*, *619*, *621*); (ii) $M(CO)_4LL$ (LL = 2,2′-bipyridyl, 1,10-phenanthroline, M = Mo, W) (*609*, *621*); (iii) $W(CO)_4L_2$ (L = piperidine, pyridine, L_2 = ethylenediamine) (*609*); (iv) $Cr(CO)_4LL$ (LL = 2,2′-bipyridyl) (*291*); and (v) $ClRe(CO)_3LL$ (LL = 1,10-phenanthroline, 2,2′-bipyridyl) (*623*). The emission of the $W(CO)_5L$ complexes consists of a broad band centred at about 533 nm. Although the band maximum varies little, the emission lifetime is more sensitive to the nature of the ligand (0.65–25.5 μsec). The lack of emission from the corresponding $Cr(CO)_5L$ and $Mo(CO)_5L$ complexes led the authors to assign the bands to a *d-d* triplet–singlet transition (*621*) ($^3E \rightarrow {}^1A_1$).† The emission of the $M(CO)_4LL$ complexes (LL = bidentate heterocycle) can be observed at room temperature in the solid and was assigned to a

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† Compare Section II: Only the $W(CO)_5L$ complexes show a singlet–triplet absorption. Such transitions are more intense in the W complexes because of spin-orbit coupling.

M → L(π*) transition (*609, 291*). The quantum yield for emission varies from 0.02 to 0.09. On the other hand, the luminescence of $W(CO)_4L_2$ (L = aliphatic amine, pyridine), which was at much longer wavelength, was again assigned to a *d-d* triplet–singlet transition.

Kaizu *et al.* (*291*) have associated luminescence with complexes that are photostable. Since the lowest-energy excited state of $Mo(CO)_4$-bipy has Mo → bipyridyl CT character, this complex fulfills the requirement particularly well. Wrighton has noted that a number of complexes that dissociate (*618*) rapidly in solution at room temperature, luminesce at 77°K, but no longer dissociate. However, considerably more evidence is needed before a detailed theory of the luminescence of these compounds can be formulated.

The series of Re complexes $ClRe(CO)_3LL$ have much higher emission quantum yields (at 77°K, $\Phi \simeq 0.3$) than the Group VIB complexes and are the first known examples of transition metal carbonyls that luminesce in fluid solution (*609*). The emission is assigned to a triplet–singlet M → L(π*) CT transition. Complexes that emit in solution should be useful for studies of energy transfer and nonradiative decay.

C. Flash Photolysis

Flash photolysis is one of the most important techniques for investigating short-lived electronically excited molecules as well as reactive species. With a light flash of about 10^{-6} (conventional flash lamps) (*413, 449*) or 10^{-9} sec (laser flash) (*414*) duration, a relative high concentration of transients is produced. A detailed description of the technique can be found in the literature (*51, 448*). Ultraviolet absorption spectroscopy is the normal method of characterizing the transients. Ultraviolet spectra of organometallics are often poorly resolved and assignment of bands of stable molecules is already difficult; flash spectra are correspondingly more problematical to interpret. Infrared spectra of organometallics carry much more structural information and are more readily assigned. The development of flash apparatus with IR detection is, therefore, an important goal; it should be attained in the not too distant future. That such measurements are possible in principle has been shown by Pimentel *et al.* (*557*). The application to organometallics (e.g., metal carbonyls), which should be extremely fruitful, is hampered by the lack of a suitably transparent solvent.

Flash photolysis of metal carbonyls has been restricted mainly to chromium and iron. Photolysis of $Cr(CO)_6$ in cyclohexane yielded a highly reactive species (λ_{max}: 503 nm), assigned to $Cr(CO)_5$, which reacts rapidly with CO to re-form $Cr(CO)_6$ (*300*):

$$Cr(CO)_5 + CO \longrightarrow Cr(CO)_6$$
$$[k = (3 \pm 1) \times 10^6 \text{ liters mole}^{-1} \text{ sec}^{-1}]$$

The observation that this reaction proceeds much faster ($k \sim 3.5 \times 10^8$ liters mole^{-1} sec^{-1}) in perfluoromethylcyclohexane (*301*) points toward a considerable interaction between $Cr(CO)_5$ and cyclohexane. Such effects were previously observed in matrix studies (*229*).

$$Cr(CO)_6 + \text{solvent} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Cr(CO)_5 \cdot (\text{solvent})$$

By laser flash photolysis the interaction of a variety of organic solvents ($\sim 10^{-2}$ *M* in cyclohexane) with $Cr(CO)_5$ could be studied directly (*298*). The rate constants for the formation and the stability constants of $Cr(CO)_5L$ have been deduced (see Table IV).

Constant k_1 appears to be a direct measure of the ability of a potential ligand to occupy a "relatively free" coordination site. Rate constants such as k_1 may be of some use as parameters describing solvent effects in organometallic reactions involving free coordination sites (*298*).

Earlier results, which were interpreted in terms of the formation of a $Cr(CO)_5$ unit with D_{3h} symmetry (trigonal bipyramid) from the initial C_{4v} $Cr(CO)_5$ (square pyramid) (*396*), now appear to be due to traces of impurities in the solvents. An alternative suggestion that the primary species observed in solution is an isocarbonyl $(OC)_5Cr \cdot OC$ (*609*) cannot be reconciled with the observed kinetics.

TABLE IV

RATE CONSTANTS AND STABILITY CONSTANTS FOR THE REACTION OF $Cr(CO)_5$ WITH L[a]

L	k_1 (liters mole^{-1} sec^{-1})	k_2 (sec^{-1})	K[b] (liters mole^{-1})	λ_{max}(nm) for $Cr(CO)_5L$[c]
Benzene	7.0×10^6	2.1×10^5	3.4×10^1	475
Diethyl ether	1.1×10^7	1.4×10^2	7.6×10^4	455
Methanol	3.1×10^7	—	—	460
Ethyl acetate	9.2×10^7	8.1×10^1	1.1×10^6	445
Acetone	1.3×10^8	1.4×10^1	9.3×10^6	438
Acetonitrile	1.6×10^8	$< 1 \times 10^{-2}$	$< 1 \times 10^{10}$	391

[a] Data from Kelly *et al.* (*298*).

[b] K = equilibrium constant (k_1/k_2).

[c] Measurements ± 5 nm.

A recent study concerned with the flash photolysis of $Fe(CO)_5$ (*299*), shows that in this case, too, the first step is probably the elimination of CO yielding $Fe(CO)_4$. Using cyclohexane as solvent, substantial amounts of $Fe_3(CO)_{12}$ were formed. The differences in the behavior of $Fe(CO)_4$ and $Cr(CO)_5$ may be due to different ground-state multiplicities. Although $Cr(CO)_5$ should have a singlet ground state (*96b*), a triplet ground state appears to be most probable for $Fe(CO)_4$ (C_{2v} symmetry) (*445*). The symmetry-allowed combination of triplet–$Fe(CO)_4$ units to $Fe_2(CO)_8$ [which has already been identified in the matrix (*444*)] and the insertion of $Fe(CO)_4$ into $Fe_2(CO)_8$ provide a reasonable pathway for the rapid formation of $Fe_3(CO)_{12}$.

Photodecomposition of $Ni(CO)_4$ in the gas phase, leading to the successive loss of CO groups, was studied by flash photolysis as early as 1961 (*102*). In the presence of oxygen, decomposition of $Ni(CO)_4$ and $Fe(CO)_5$ is initiated by the flash, followed by slow heterogeneous oxidation (*103*). The same authors reported spectra of excited atoms (Fe and Ni) and excited ions, produced by isothermal flash photolysis of $Ni(CO)_4$ and $Fe(CO)_5$ (*104, 105*).

In 1967, a Canadian group (*569*) described the flash photolysis of cyclobutadiene tricarbonyliron in the gas phase, using a fast-response mass spectrometer for detection of short-lived transients. In this way they observed the fragments ($C_4H_4{}^+$) and [$Fe(CO)_3{}^+$] and proposed the elimination of C_4H_4 as the major primary photolytic step (*204*):

$$(C_4H_4)Fe(CO)_3 \xrightarrow{h\nu} C_4H_4 + Fe(CO)_3$$

The same group studied photolysis of cyclobutadiene tricarbonyliron in a matrix and observed an intense ESR signal, attributed to $Fe(CO)_3$. These authors suggested that the elimination of C_4H_4 was also the primary step in the matrix, a result that was recently doubted by Chapman *et al.* (*110*) (see Section III, D).

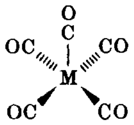
The method of using a kinetic mass spectrometer as a detector for flash photolysis was also employed for the photoreaction of $Fe(CO)_5$ in presence of NO (*544*). In addition to the known stable compound $Fe(CO)_2(NO)_2$, the unstable neutral species $Fe(CO)(NO)_3$ was observed. The latter compound, which does not follow the noble gas rule, decays with a half-life of ~ 75 msec.

D. PHOTOLYSIS IN RIGID MEDIA

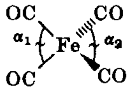
The aim of the matrix isolation technique is to embed individual molecules of a compound in a large excess of host material. This matrix, which is usually produced by cocondensation of host and reactant, is typically solid argon; temperatures are in the range of 4° to 20°K. The isolated compounds are examined by spectroscopic methods, chiefly by UV and IR absorption spectroscopy. Unstable species may be produced by photolysis of the molecules deposited in the matrix, thus allowing the direct observation of many primary products of photochemical reactions which cannot be detected by other means. For detailed information on the method, the interested reader is referred to the literature (*247*, *172*, *382*).

1. *Matrix Photochemistry of Binary Metal Carbonyls*

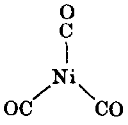
Metal carbonyls are especially suitable for matrix isolation and have been investigated extensively. The high extinction coefficient of the CO-stretching vibration in M(CO) moieties facilitates the observation of reactions. According to current evidence the first observable effect on photolysis of an unsubstituted metal carbonyl is the loss of a carbon monoxide molecule. Typical examples investigated are $M(CO)_6$ [M = Cr, Mo, W], $Fe(CO)_5$, $Ni(CO)_4$, and $Fe_2(CO)_9$ (*230*, *231*, *442*, *444*, *445*, *469*, *471*). The primary species observed are compounds **19–23**.



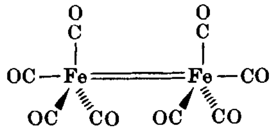
C_{4v}
(M = Cr, Mo, W)
(**19**)



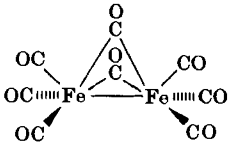
C_{2v}
(α_1 = 147°; α_2 = 120°)
(**20**)



D_{3h}
(**21**)



C_{2v}
(**22**)



D_{3d}
(**23**)

By comparing the spectra of ^{13}CO-enriched fragments with calculated spectra, the structures can be determined much more reliably than from the ^{12}CO spectra alone (*430*). This technique has been applied, for instance, to $Fe(CO)_4$ (*445*). Further photolysis can produce secondary products such as $M(CO)_4$ (M = Cr, Mo, W) and $M(CO)_3$ (M = Fe, Cr, Mo, W) (*492*, *441*).

a. Group VIB Carbonyls. The data for $M(CO)_5$ are collected in Table V. The reader may ask why $Cr(CO)_5$ does not react back immediately to $Cr(CO)_6$. In fact this back reaction needs further activation

TABLE V

INFRARED FREQUENCIES FOR $M(CO)_5$ ($M = Cr, Mo, W$) IN DIFFERENT MATRICES[a]

Cr(*230*) Ar (cm^{-1})	Cr(*428*) Xe (cm^{-1})	Cr(*429*) Ar + 2% Xe[b]		Mo(*230*) Ar (cm^{-1})	W(*230*) Ar (cm^{-1})	Assignment
		Xe (cm^{-1})	Ar (cm^{-1})			
2093	2086	2089	2092	2098	2097	A_1
1936	1929	1939	1936	1933	1932	A_1
1966	1956	1963	1965	1973	1963	E

[a] References are given in parentheses in column heads.

[b] Columns labeled Xe and Ar give frequencies for $Xe \cdots Cr(CO)_5$ and $Ar \cdots Cr(CO)_5$, respectively, in an Ar + 2% Xe matrix.

(*230*) and occurs rapidly upon illuminating the matrix with wavelengths corresponding to the visible absorption of $Cr(CO)_5$. The back reaction is also observed when Ar matrices are doped with 1% CO and warmed to 45°K. Two explanations have been offered for the effect of visible light: (a) a local annealing of the matrix upon radiationless dissipation of the energy absorbed and (b) a specific photoreaction. We will return to this point later.

Although the matrix material has no major effect on the infrared spectra of $Cr(CO)_5$, a remarkable dependence of the long-wavelength UV absorption on the matrix was observed (*229*, *429*) (Table VI). In

TABLE VI

VISIBLE ABSORPTION BANDS OF $Cr(CO)_5$ IN DIFFERENT MATRICES[a]

Matrix	Band maxima (nm)	Band maxima (10^3cm^{-1})
Ne	624	16
SF_6	560	17.1
CF_4	547	18.3
Ar	533	18.8
Kr	518	19.3
Xe	492	20.3
CH_4	489	20.4
CO	462	21.6
Ne/Xe	628	15.9
	487	20.5

[a] Data from R. N. Perutz and J. J. Turner (*429*).

two-component matrices (x and y) both species $x\cdots \mathrm{Cr(CO)_5}$ and $y\cdots \mathrm{Cr(CO)_5}$ can be observed, thus demonstrating a specific interaction between the fragment and the matrix species, which is significant even for noble gas atoms. The interacting matrix species can be exchanged by selective photolysis:

$$x\cdots \mathrm{Cr(CO)_5} \underset{h\nu\,(2)}{\overset{h\nu\,(1)}{\rightleftharpoons}} y\cdots \mathrm{Cr(CO)_5}$$

By considering a simple d-orbital scheme for C_{4v} $\mathrm{Cr(CO)_5}$ (*615*) (Fig. 7), it can be predicted that ΔE in $\mathrm{Cr(CO)_5}$ will be increased by a ligand L approaching the system in the z direction. This will result in a shift of the longest-wavelength d-d transition to shorter wavelength (*128*). The change in the visible spectrum has been attributed to interaction of this type and a change in the axial-radial bond angle of $\mathrm{Cr(CO)_5}$. (The IR spectra of species $x\cdots \mathrm{Cr(CO)_5}$ and $y\cdots \mathrm{Cr(CO)_5}$ also differ appreciably. The bond angles are calculated from relative intensities of IR bands (*429*).)

The significant change in the $\mathrm{Cr(CO)_5}$ absorption between $\mathrm{CF_4}$ and $\mathrm{CH_4}$ matrices suggests that the latter interacts much more strongly. Occupation of a vacant coordination site by a hydrocarbon is a matter of current interest (*126*). Attempts to correlate the structural parameters with the degree of interaction may help toward an understanding of C—H activation by transition metal compounds.

Returning to the effect of light on the recombination of CO with $\mathrm{Cr(CO)_5}$, Turner *et al.* (*96a*, *428*) report experiments that clarify this behavior. By using polarized light, they have been able to produce oriented $\mathrm{Cr(CO)_5}$ in $\mathrm{CH_4}$ matrices. They showed that $\mathrm{Cr(CO)_5}$ could undergo photochemically induced reorientation in a matrix. These results may be explained by a D_{3h} structure of the excited $\mathrm{Cr(CO)_5}$ that can return to the C_{4v} ground state in several orientations by undergoing a Berry twist (*393*), so producing an apparent rotation. Recent calculations support this suggestion (*96*, *96b*). This mechanism (Fig. 8) also

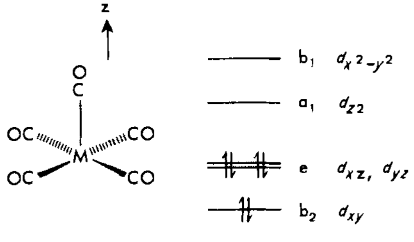


FIG. 7. d-Orbital splitting diagram for C_{4v} $\mathrm{Cr(CO)_5}$.

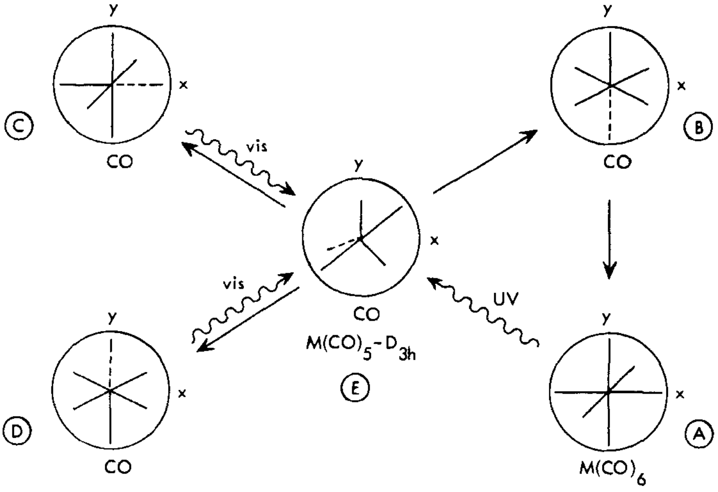


FIG. 8. Proposed mechanism of reactions of C_{4v} Cr(CO)$_5$. Central D_{3h} species represents postulated first-excited state of M(CO)$_5$. Symbols x and y indicate different matrix atoms. Diagram shows generation of M(CO)$_5$ from M(CO)$_6$ (A → E → C and A → E → D), exchange of matrix atoms in vacant site of M(CO)$_5$ (C → E → D), rotation of M(CO)$_5$ (C → E → D), and recombination of M(CO)$_5$ with CO (C → E → B → A and D → E → B → A).

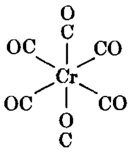
explains the photochemical recombination of Cr(CO)$_5$ with CO and the photochemical exchange of the interacting matrix species.

The intermediacy of D_{3h} Cr(CO)$_5$ also allows the rationalization of the escape of the released CO on initial photolysis of Cr(CO)$_6$:

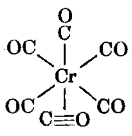
$$\mathrm{Cr(CO)_6} \xrightarrow{h\nu} \mathrm{Cr(CO)_6^*} \xrightarrow{-\mathrm{CO}} \underset{C_{4v}}{\mathrm{Cr(CO)_5^*}} \longrightarrow \underset{D_{3h}}{\mathrm{Cr(CO)_5^*}} \longrightarrow \underset{\text{reoriented } C_{4v}}{\mathrm{Cr(CO)_5}}$$

However, in some cases local annealing of the matrix may be a valid explanation.

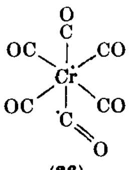
Another interesting problem is posed by the formation of Cr(CO)$_5$ in a pure CO matrix. The absorption maximum at 462 nm in CO matrices demonstrates that this species is different from all others observed (see Table VI) (*430*). There has been considerable discussion as to whether the CO interacts with the free coordination site of Cr(CO)$_5$ via oxygen (**24**) or sideways (**25**) (*96c*, *354*, *430*, *609*).



(24)



(25)



(26)

We would like to introduce an additional suggestion. This is the formation of species (**26**), which may result either from the addition of CO to an excited $Cr(CO)_5$ molecule or from "incomplete bond rupture" in $Cr(CO)_6$. A fast thermal reversal of (**26**) to $Cr(CO)_6$ may be inhibited by the interaction of this species with CO in the matrix.

There have been several reports in the literature of the existence of a D_{3h} form of $M(CO)_5$; however, all these observations have been questioned. Sheline was the first to report a D_{3h} form of $M(CO)_5$ (*542*, *543*) claiming that it resulted from warming up glasses containing C_{4v} $Mo(CO)_5$. Braterman *et al.* (*67*) as well as Turner *et al.* (*229*) showed that formation of the "Sheline D_{3h}" was dependent on the concentration of $M(CO)_6$ and was probably the result of a species of the composition $M(CO)_6$–$M(CO)_5$. More recently, Ozin (*354*) claimed to have observed a very stable D_{3h} $Cr(CO)_5$, resulting from the cocondensation of chromium atoms and CO in CO/Ar matrices. Turner *et al.* (*96c*) have suggested that the spectra observed by Ozin can be reassigned to a mixture of two C_{4v} species [$(OC)_5Cr\cdots Ar$ and $(CO)_5Cr\cdots CO$, see above) together with $Cr(CO)_4$.

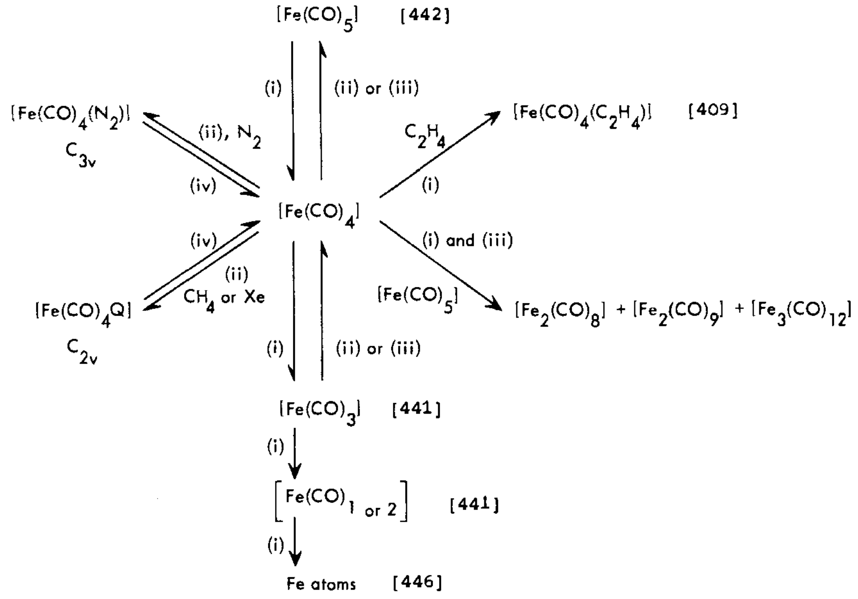
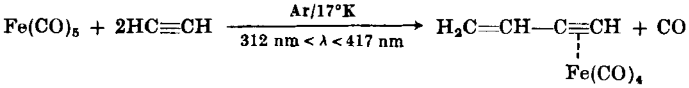


FIG. 9. Principal reactions of matrix-isolated $Fe(CO)_4$. (i) Ultraviolet photolysis; (ii) "Nernst-glower" photolysis ($\lambda > 320$ nm); (iii) annealing matrix; (iv) $\lambda > 375$ nm. [From Poliakoff and Turner (*445*).]

b. $Fe(CO)_5$ *and* $Fe_2(CO)_9$. Extensive work on $Fe(CO)_5$ (*442, 443, 441, 446, 445*) has led to the final conclusion that the primary product on photolysis is C_{2v} $Fe(CO)_4$. ^{13}CO Exchange experiments support this result. On the basis of MO calculations (*96*), a triplet ground state is suggested for $Fe(CO)_4$. (For an extensive report on the photochemistry of $Fe(CO)_5$, see Ref. *331*.)

The principal reactions of matrix-isolated $Fe(CO)_4$ are summarized in Fig. 9 (*445*).

Ogilvie *et al.* (*409*) provided the first evidence for the formation of an ethylene complex and also proposed a 1-butene-3-yneiron complex:



$$Fe(CO)_5 + 2HC{\equiv}CH \xrightarrow[312\text{ nm} < \lambda < 417\text{ nm}]{Ar/17°K} H_2C{=}CH{-}\underset{\underset{Fe(CO)_4}{\vdots}}{C}{\equiv}CH + CO$$

Photolysis of $Fe_2(CO)_9$ in matrices at 20°K yielded $Fe_2(CO)_8$ in two isomeric forms, probably **22** and **23** [see page 84 (*444*)]. This finding is of special interest for the understanding of the behavior of $Fe(CO)_4$ in solution. Compound **22** may be the key intermediate in the rapid formation of $Fe_3(CO)_{12}$ (see Section III, C) as well as in many other reactions (*201*).

2. *Matrix Photochemistry of Substituted Metal Carbonyls*

As discussed in Section IV, other photoprocesses have to be considered for substituted metal carbonyls apart from the elimination of CO. Unfortunately, as Braterman (*49, 50*) has explained, only a few of these reactions can be observed directly in the matrix.

a. Group VIB Metal Carbonyl Compounds. Although the photolysis of bis(triisopropylphosphine) tetracarbonyltungsten in solution under a CO atmosphere gives rise to the dissociation of the M—P bond,

$$W(CO)_4P_2 \xrightarrow{h\nu/CO} W(CO)_5P$$

the corresponding fragment is observed neither in a hydrocarbon nor in a methyl tetrahydrofuran glass (*49*). Dissociation of the metal–phosphine bond in the matrix may escape detection because of rapid recombination in the cage. Diffusion of such large species is extremely limited in the matrix. In the light of the observations by Turner *et al.* (*96a*), it remains an open question whether steric and/or electronic factors control the reorientation of an intermediate to a position where the free coordination site is removed from the expelled ligand. The largest ligand that has been observed to dissociate from a metal carbonyl molecule in a hydrocarbon glass is PH_3 from $Mo(CO)_5PH_3$ (*49*). Irradiation of $Mo(CO)_5P(C_6H_{11})_3$ at 77°K with $\lambda > 305$ nm in a hydrocarbon glass yields two isomers, whereas in methyl tetrahydrofuran only the cis isomer is formed (*50*). The reaction is described in Fig. 10. Such isomerization has also been observed for the species $Cr(CO)_4CS$ generated from $Cr(CO)_5CS$ in an Ar matrix. In this case both cis → trans and trans → cis isomerization have been observed (*440*).

b. Manganese Compounds. Photolysis of $HMn(CO)_5$ in Ar at 15°K results in loss of CO and formation of $HMn(CO)_4$. Upon irradiation with $\lambda > 285$ nm, the reaction is reversed (*470*):

$$HMn(CO)_5 \underset{h\nu/\lambda > 285\ nm}{\overset{h\nu/\lambda = 229\ nm}{\rightleftharpoons}} HMn(CO)_4$$

The photochemical reactions of $XMn(CO)_5$ ($X = CH_3, CH_3CO, CF_3$) were investigated by Ogilvie (*417*) and Rest (*468*). The results of Rest are summarized as follows:

$$\begin{tikzcd}
CH_3COMn(CO)_5 \arrow[r, "h\nu/-CO", "300\ nm < \lambda < 600\ nm"'] & CH_3COMn(CO)_4 \arrow[r, "h\nu", "\lambda > 320\ nm"'] & CH_3Mn(CO)_5 \arrow[d, shift right, "h\nu\ 230\ nm < \lambda < 280\ nm"'] \\
& & CH_3Mn(CO)_4 + CO \arrow[u, shift right, "h\nu/\lambda > 280\ nm"']
\end{tikzcd} \qquad (3)$$

The primary process in $CH_3COMn(CO)_5$ is the loss of a terminal CO (probably equatorial) and corresponds well with solution photochemistry (*410*).

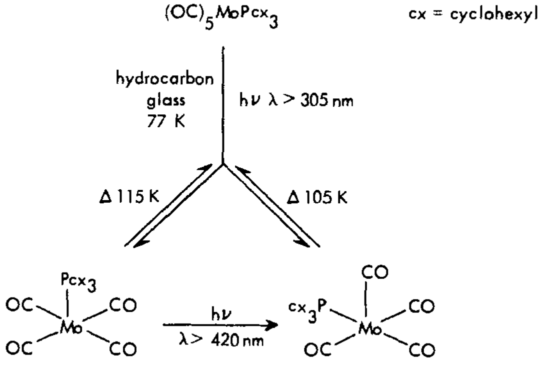


FIG. 10. Photochemical formation of cis and trans isomers of $(CO)_4MoPcx_3$ from $(CO)_5MoPcx_3$. [From Black and Braterman (*50*).]

The cyclopentadienyl carbonylmanganese complexes lose CO on photolysis and are regenerated upon softening the glass (*69*)†:

$$(\pi\text{-}\mathrm{RC_5H_4})\mathrm{Mn(CO)_3} \underset{\Delta}{\overset{\substack{h\nu \\ \text{methylcyclohexane } 80\,\mathrm{K}}}{\rightleftharpoons}} (\pi\text{-}\mathrm{RC_5H_4})\mathrm{Mn(CO)_2} + \mathrm{CO}$$

$(\mathrm{R} = \mathrm{H, CH_3})$

Carbon monoxide is also eliminated (*467*) on photolysis of $\mathrm{Mn(CO)_4NO}$:

$$\begin{tikzcd}
\mathrm{Mn(CO)_4NO} \arrow[r, shift left, "\substack{h\nu \\ \mathrm{Ar},\ 15^\circ\ \mathrm{K}/h\nu\ (280\ \mathrm{nm} < \lambda < 360\ \mathrm{nm})}"] & \mathrm{Mn(CO)_3NO} + \mathrm{CO} \arrow[l, shift left, "h\nu\ (\lambda > 550\ \mathrm{nm})"] \arrow[d, shift right, "\substack{h\nu \\ (230\ \mathrm{nm} < \lambda \\ < 280\ \mathrm{nm})}"'] \\
 & \mathrm{Mn(CO)_2NO} + \mathrm{CO} \arrow[u, shift right, "\Delta\ (30^\circ\mathrm{K})"']
\end{tikzcd}$$

c. *Iron Carbonyl Compounds.* Some controversy exists about the matrix photochemistry of cyclobutadiene tricarbonyliron. Gunning *et al.* (*569*) claimed on the basis of ESR evidence that $\mathrm{Fe(CO)_3}$ was formed on photolysis ($\lambda > 220$ nm) at 77°K, both in the solid compound and in matrices of $\mathrm{C_3F_8}$ and neopentane. However, Chapman (*110*) has shown in IR experiments that the only process at 8°K is the loss of CO. Chapman's observations are supported by the behavior of $\mathrm{(C_4H_4)Fe(CO)_3}$ in solution. Photosubstitution of one CO by olefin is possible (*594*), and one or two CO groups have been substituted by phosphine (*201*). It was shown that the quantum yield for CO loss is at least 10 times larger than the quantum yield for the loss of cyclobutadiene (*201*).

3. *Photochemistry in Reactive Matrices*

When transition metal compounds are photolyzed in matrices consisting of material that can react to form primary products, two types of compounds may be formed. (a) Species normally not observed because of rapid recombination are detectable by reaction with the matrix; (b) unstable compounds not otherwise accessible can be produced.

In pure CO matrices, photolysis of carbonyl nitrosyls leads to substitution of NO by CO, thus demonstrating the cleavage of a metal–NO bond that is otherwise not observed (*132*, *134*) [in Ar or $\mathrm{CH_4}$ the loss of CO is the only detectable process (*132*, *134*)]. The substitution of π-bonded ligands has also been achieved (*134*):

$$\mathrm{Fe(CO)_2(NO)_2} \xrightarrow[\text{CO matrix}]{h\nu} \mathrm{Fe(CO)_5} + \mathrm{NO}$$

---

† Some interesting observations in an Apiezon *N*-matrix are found in Ref. *49*.

$$\mathrm{Co(CO)_3(NO)} \xrightarrow[\text{CO matrix}]{h\nu} \mathrm{Co(CO)_4 + NO}$$

$$(\pi\text{-}\mathrm{C_5H_5)NiNO} \xrightarrow[\text{CO matrix}]{h\nu} (\pi\text{-}\mathrm{C_5H_5)Ni(CO)_2} \xrightarrow{h\nu} \mathrm{Ni(CO)_4}$$

$$\mathrm{Mn(CO)_4NO} \xrightarrow[\text{CO matrix}]{h\nu} \mathrm{Mn(CO)}_x + \mathrm{NO} \qquad (x = 5 \text{ or } 6)$$

Metal carbonyl nitrosyls can be produced by photolysis of carbonyls in NO-doped Ar matrices (*132, 134*):

$$\mathrm{Fe(CO)_5} \xrightarrow[\text{Ar/NO matrix}]{h\nu} \mathrm{Fe(CO)_2(NO)_2}$$

$$\mathrm{Os(CO)_5} \xrightarrow[\text{Ar/NO matrix}]{h\nu} \mathrm{Os(CO)_2(NO)_2}$$

Irradiation of $Fe(CO)_5$ and $Ni(CO)_4$ in nitrogen matrices results in CO substitution by N_2 (*443, 445*), yielding, for instance, $Ni(CO)_3N_2$ (*466*).

In carbonyl nitrosyl compounds, the substitution of CO by N_2 can also be observed (*134*):

$$\mathrm{Co(CO)_3NO} \xrightarrow[\mathrm{N_2}\text{ matrix}]{h\nu} \mathrm{Co(CO)_2(NO)N_2 + CO}$$

4. *Ionic Carbonyls in Matrices*

Heterolytic cleavage of metal CO bonds can be achieved by vacuum UV photolysis (H_2 or Ar arc) (*95, 72a*). In this way anions $Ni(CO)_3^-$, $Cr(CO)_5^-$, and $Fe(CO)_4^-$ have been detected. In the case of $Ni(CO)_4$, CO^+ has been observed, but the other cations have not yet been positively identified. Vacuum UV photolysis of $V(CO)_6$ results in formation of $V(CO)_6^-$. The mechanism of these reactions is still under investigation. Heterolytic cleavage according to

$$(\pi\text{-}\mathrm{C_5H_5)NiNO} \xrightarrow{h\nu} (\pi\text{-}\mathrm{C_5H_5)Ni^+ + NO^-} \qquad (4)$$

has been claimed for (π-C_5H_5)NiNO on UV photolysis (*133, 134*). The anionic species $Cr(CO)_5^-$, $Co(CO)_3NO^-$, and $Co(CO)_4^-$ can also be produced by incorporation of alkali metal atoms in matrices and subsequent photolysis (*72*) or by electron bombardment during deposition (*72a*):

$$\mathrm{Cr(CO)_6} \xrightarrow[h\nu]{\text{Na/Ar}} \mathrm{Cr(CO)_5^- + Na^+}$$

The anion $V(CO)_6^-$ has also been photolyzed in a MeTHF glass at 77°K and formation of $[V(CO)_5MeTHF]^-$ has been observed (*67*).

In recent years, matrix photochemistry has turned out to be the most powerful means of elucidating structures of intermediates in metal carbonyl photochemistry. The structures are less symmetrical than had been anticipated (*227*, *303*) and have required the development of new theoretical approaches (*96*, *96b*). The application of matrix isolation to compounds less favorable than organometallics has been little explored and should profit from the advent of Fourier-transform IR spectroscopy. Processes that are observed in the matrix probably also occur in solution. However, processes not detectable in the matrix should also be considered in solution. The reviewers feel that a comparative study of systems by matrix and flash photolysis will be a rewarding approach.

E. QUENCHING AND SENSITIZATION PROCESSES IN ORGANO-TRANSITION-METAL PHOTOCHEMISTRY

In this section we will briefly survey quenching processes in which organometallic compounds are involved. We will consider quenching processes as those bimolecular processes in which an electronically excited compound A* interacts with a ground-state molecule B. We will distinguish three cases:

(a) A* = organic; B = organometallic
(b) A* = organometallic; B = organic
(c) A* = organometallic; B = organometallic

The major modes of quenching are as follows:

1. Electronic energy transfer, e.g., according to the general scheme (*358*),

$$A^* + B \longrightarrow A + B^*$$

2. Formation of excited complexes (*exciplex*),

$$A^* + B \longrightarrow (AB)^*$$

3. External heavy atom effect,† whereby the interaction of heavy atoms with the excited molecule A* may enhance radiationless deactivation via spin-forbidden processes by inducing spin-orbit coupling externally.

$$^1A^* \xrightarrow{M_{(\text{heavy})}} {}^3A^*$$

or

$$^3A^* \xrightarrow{M_{(\text{heavy})}} {}^1A$$

4. Electron transfer processes, e.g.,

$$A^* + B \longrightarrow A^{\cdot +} + B^{\cdot -}$$

5. Quenching by chemical processes, e.g.,

$$(ML_n)^* + L' \longrightarrow [L'ML_n] \longrightarrow ML'L_{(n-1)} + L$$

---

† Another bulk property of metal-containing systems that is probably of some importance in quenching processes is the so-called spin-catalyzed deactivation. For detailed information see Refs. *51* and *55*.

The example given would be typical of quenching by a bimolecular chemical process. It should be noted that electron transfer can be considered as a special case of chemical quenching.

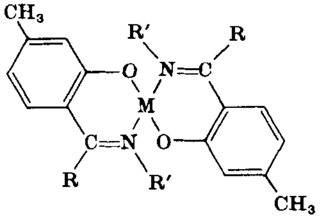
A very critical and detailed discussion of quenching and sensitization processes of *coordination compounds* can be found in the literature (*28*). A more extensive discussion of quenching processes involving organometallics than is possible in the present review will be given elsewhere (*55*). We will restrict ourselves here to the discussion of a few examples illustrating the principles outlined above.

1. Electronic Energy Transfer

One of the most commonly used sensitizers in organic photochemistry is triplet-excited benzophenone. It is therefore, not surprising that the first attempts to sensitize photochemical reactions of transition metal carbonyls were carried out with benzophenone. Vogler (*586*) irradiated $Cr(CO)_6$ and benzophenone and then added pyridine. He concluded that triplet energy transfer had occurred from benzophenone to $Cr(CO)_6$, leading to $Cr(CO)_5$. The limiting quantum yield of the process was determined to be unity.

Diffusion-controlled quenching of triplet fluorenone (k_q = 3–8 × 10^9 liters $mole^{-1}$ sec^{-1}) by iron carbonyl complexes with olefins, dienes, and α,β-unsaturated ketones and by some sandwich complexes has been attributed to a triplet-triplet energy transfer (*226*).

The quenching of a variety of triplet-excited organic molecules (benzophenone, triphenylene, phenanthrene, 2-acetonaphthone, chrysene, pyrene, 1,2-benzanthracene, anthracene) by Ni(II) and Pd(II) chelates of the general structure **27** has been studied by Wilkinson *et al.* (*8, 1, 606*).



(27)

R	R′
CH_3	OH
$C_{11}H_{23}$	OH
CH_3	OBu
CH_3	Bu

Slightly different rates for the quenching of high- and of low-energy triplet donor molecules by these complexes have been explained by two different energy-transfer processes. The high-energy donors are quenched by energy transfer to intraligand π-π^* states [benzophenone–NiL_2 ($R = CH_3$, $R' = OH$): $k_q = 5.9 \times 10^9$ liters $mole^{-1}$ sec^{-1}], whereas ligand field states of the acceptors are initially produced in the case of low-energy triplet donors [anthracene–NiL_2 ($R = CH_3$, $R' = OH$): $k_q = 3.6 \times 10^9$ liters mole^{-1} sec^{-1}]. Although for the first transfer, orbital overlap is not critical, the latter process requires good overlap of the metal *d* orbitals with the donor molecule. Here the energy-transfer efficiency can be affected by changing the geometry of the complexes, e.g., by variation of the ligands in the nickel(II) chelates.

These examples demonstrate energy transfer from excited organic molecules to an organometallic system; the following reactions are examples for the reverse reaction.

Electronically excited $[Ru(bipy)_3]^{2+}$ is quenched by *trans*-stilbene, *trans*-2-styrylpyridine, *trans*-4-styrylpyridine, and anthracene (*610a*) (Φ *trans* → *cis*-styrylpyridine = 0.4; Φ *trans* → *cis*-stilbene ~ 0.5). Large amounts of cis isomers ($> 90\%$) are found in the photostationary state achieved by this energy-transfer process, both in the case of stilbene and styrylpyridines. This result is consistent with a donor triplet energy below 57 kcal/mole (E_T *cis*-olefin = 57 kcal/mole; E_T *trans*-olefin = 49–50 kcal/mole); *cis*-pentadiene (E_T = 57 kcal/mole) does not show any quenching activity.

An interesting example for energy transfer from an organometallic to an organic substrate and vice versa is the intramolecular energy transfer observed with several metalloporphyrin complexes (M = Mg, Zn, Co), containing azastilbene ligands (L) (*604*). The remarkably efficient cis-trans isomerizations of stilbazole coordinated to Zn etioporphyrin ($\Phi = 0.4$), Mg etioporphyrin ($\Phi = 0.17$), and especially of 1-(1-naphthyl)-2-(4-pyridyl)ethylene (NPE) coordinated to Zn etioporphyrin ($\Phi = 6.6$) and Mg etioporphyrin ($\Phi = 3$) have been interpreted by the following mechanism:

$$\mathrm{MP{-}L} \longrightarrow {}^{1}\mathrm{MP^{*}{-}L} \longrightarrow {}^{3}\mathrm{MP^{*}{-}L} \tag{5}$$

$$ {}^{3}\mathrm{MP^{*}{-}L} \longrightarrow \mathrm{MP{-}{}^{3}L^{*}} \longrightarrow \mathrm{MP{-}{}^{3}L'^{*}} \tag{6}$$

$$\mathrm{MP{-}{}^{3}L'^{*}} \longrightarrow \alpha\mathrm{MP{-}L'} + (1-\alpha)\mathrm{MP{-}L} \tag{7}$$

$$\mathrm{MP{-}{}^{3}L'^{*}} \longrightarrow {}^{3}\mathrm{MP^{*}{-}L'} \tag{8}$$

$$ {}^{3}\mathrm{MP^{*}{-}L'} + \mathrm{L} \longrightarrow {}^{3}\mathrm{MP^{*}{-}L} + \mathrm{L'} \tag{9}$$

$$ {}^{3}\mathrm{MP^{*}{-}L} \longrightarrow \mathrm{MP{-}L} \tag{10}$$

$$ {}^{3}\mathrm{MP^{*}{-}L'} \longrightarrow \mathrm{MP{-}L'} \tag{11}$$

(L = cis isomer, L′ = trans isomer)

In the primary photoprocess, a porphyrin-localized triplet state is produced [Eq. (5)], which undergoes intramolecular energy transfer, leading to an olefin-localized triplet state [Eq. (6)]. This species is expected to be able to undergo isomerization. The resulting isomerized molecule, which is still in a ligand-localized excited state, can either decay to a mixture of the ground-state molecules [Eq. (7)] or undergo reversible intramolecular energy transfer [Eq. (8)], leading back to a porphyrin-localized triplet state, now containing a *trans*-olefin ligand. The authors postulate that this species should be capable of ligand exchange during its lifetime [Eq. (9)]. (The reader can only admire the patience of the porphyrin molecule!) The regenerated but still excited starting complex must now play this game again. In the case of NPE, it has to pass through the sequence at least 6 times. It should be noted that the authors took considerable care to rule out trivial mechanisms, as for instance a chain mechanism via radical ions. The interesting point about Eq. (9) is that it describes the rare process of a bimolecular reaction of an electronically excited transition metal complex (see below).

A special case of two organometallic species, working as donor and acceptor in triplet energy transfer, is the intramolecular energy transfer from triplet-excited Zn porphyrin to a Cu porphyrin, which are linked by a —CO—NH—C_2H_4—NH—CO— chain (*522*).

Other important reports on this subject include Refs. *612, 618, 615,* and *291.*

2. *Exciplex Formation*

Quenching processes involving the intermediate formation of excited complexes can best be demonstrated for cases in which emission from the excited complexes is observed. For example (*25*),

$$\textit{cis}\text{-Ir(phen)}_2\text{Cl}_2{}^+ \xrightarrow{h\nu} ({}^1d\pi^*)\ \textit{cis}\text{-Ir(phen)}_2\text{Cl}_2{}^+ \tag{12}$$

$$({}^1d\pi^*)\ \textit{cis}\text{-Ir(phen)}_2\text{Cl}_2{}^+ \longrightarrow ({}^3d\pi^*)\ \textit{cis}\text{-Ir(phen)}_2\text{Cl}_2{}^+\cdot \tag{13}$$

$$({}^3d\pi^*)\ \textit{cis}\text{-Ir(phen)}_2\text{Cl}_2{}^+ + \text{naphthalene} \longrightarrow [\textit{cis}\text{-Ir(phen)}_2\text{Cl}_2{}^+\cdot\ \text{naphthalene}] \tag{14}$$

The formation of the exciplex [Eq. (14)] was indicated by the appearance of a new emission centered around 560 nm. Other examples have also been observed (*475, 476, 106*); they will be discussed in full elsewhere (*55*).

3. *Heavy Atom Effects*

Although quenching of excited states of transition metal complexes via heavy atom effects does not appear to be unequivocally established (*28*), it has been quite well investigated in the quenching of excited anthracene with $(CH_3)_2Hg$. The singlet-excited anthracene is quenched by $Hg(CH_3)_2$ at a diffusion-controlled rate by enhanced conversion to triplet anthracene, which is radiationlessly deactivated. The effect of $Hg(CH_3)_2$ on the latter process is small, the quenching rate of the triplet state is $k_q = 1.2 \times 10^3\ M^{-1}\ \text{sec}^{-1}$. A more detailed discussion is given in Ref. *55*.

4. *Electron-Transfer Processes*

Many processes involving transfer of electronic energy from an excited donor D to an acceptor A occur with rates close to those for diffusion control, provided that the energy of the accepting state is below that of the donor state. Usually a sharp decrease of quenching rate constants is observed when the electronic energy transfer becomes endothermic (*358*). The situation can be quite different with electron transfer, which may be exothermic, but still much slower than corresponds to diffusion control.

The principle of electron-transfer reactions can be explained using a very simple MO scheme (Fig. 11). We will return to this point later on in connection with photosynthesis (Section V, B).

Two special cases of electron-transfer quenching processes are illustrated in Fig. 11—(a) reversible electron transfer and (b) secondary electron transfer. Figure 11 may explain how electronically excited chlorophyll could be involved in electron transport phenomena (from X to A) in photosynthesis. One of the best established examples of electron transfer from an electronically excited transition metal compound to other transition metal complexes, as well as to organic

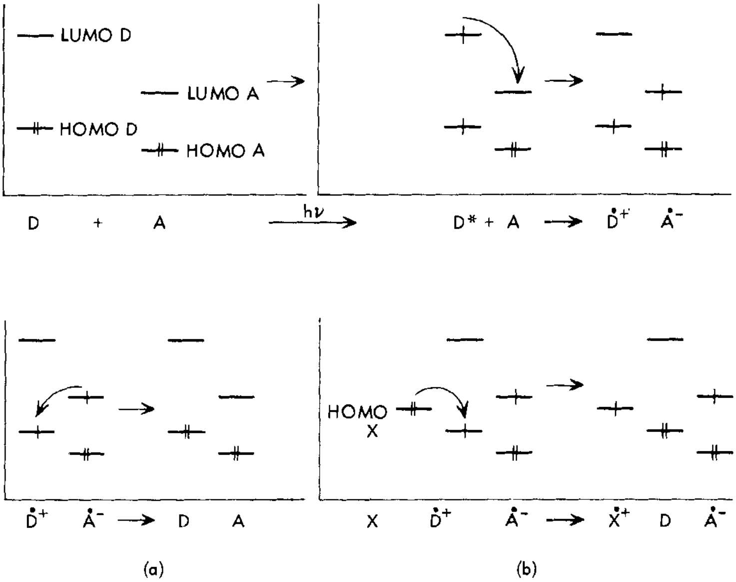


FIG. 11. Molecular-orbital scheme demonstrating electron transfer from donor molecule D to an acceptor A (upper half), reversible electron transfer (a), and secondary electron transfer from X to A (b). HOMO = highest occupied molecular orbital; LUMO = lowest unoccupied molecular orbital.

substrates, is that investigated by Bock and his collaborators (*53*). Flash spectroscopic investigation allowed the direct observation of the following processes:

$$[\mathrm{Ru(bipy)_3}]^{2+*} + \mathrm{Fe(H_2O)_6}^{3+} \xrightarrow{k_q} [\mathrm{Ru(bipy)_3}]^{3+} + \mathrm{Fe(H_2O)_6}^{2+} \qquad (15)$$

$$[\mathrm{Ru(bipy)_3}]^{3+} + \mathrm{Fe(H_2O)_6}^{2+} \xrightarrow{k_1} [\mathrm{Ru(bipy)_3}]^{2+} + \mathrm{Fe(H_2O)_6}^{3+} \qquad (16)$$

$$(k_q \sim 3 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1})$$

Similar quenching constants were observed with $[\mathrm{Ru(NH_3)_6}]^{3+}$, *trans*-1,2-bis(*N*-methyl-4-pyridyl)ethylene^{2+}, and 1,1′-dimethyl-4,4′-bipyridine^{2+}. The back reaction [Eq. (16)] occurs at a rate of approximately $10^6\ M^{-1}\ \mathrm{sec}^{-1}$, although it is exothermic ($\Delta H = -12$ kcal), but the back reaction in the case of $[\mathrm{Ru(NH_3)_6}]^{2+}$ is even faster than the corresponding forward reaction ($k_q = 2 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$, $k_1 = 3.68 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$).

Other examples of this process are found in Refs. *522*, *52*, and *362*.

5. Chemical Quenching

Photochemical ligand substitution is a very important process in organo-transition-metal chemistry, as discussed in detail in Section IV. However, quenching reactions according to the general scheme,

$$\mathrm{L}^* + \mathrm{ML}'_n \longrightarrow \mathrm{LML}'_{n-1} + \mathrm{L}'$$

$$[\mathrm{ML}'_n]^* + \mathrm{L} \longrightarrow \mathrm{LML}'_{n-1} + \mathrm{L}'$$

are not supported by well-documented examples. The $\mathrm{S_N2}$ type of reaction of $\mathrm{PPh_3}$ with $\mathrm{Mn(CO)_4NO}$ (*297*), discussed in Section IV, and the ligand-exchange reaction of the excited stilbene–porphyrin complexes (see page 95) can be considered as examples.

IV. Main Reaction Pathways in the Photochemistry of Organo-Transition-Metal Complexes

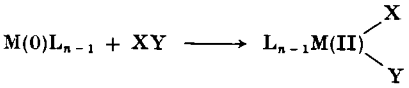
In this section the main reaction paths and mechanisms in organo-transition-metal photochemistry will be considered in more detail. In the first part we will try to survey the important types of reactions; in the second part a more explicit discussion of some additional examples is given.

A. Survey of Important Reactions in Organo-Transition-Metal Photochemistry

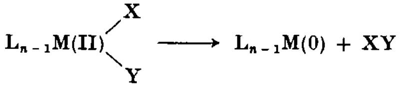
As discussed in Section III, most photoreactions of transition metal compounds result from the direct or indirect electronic excitation of *d*-*d* transitions. Reactions of CT-excited molecules are the exception rather than the rule. As pointed out in Section III, the result of *d-d* excitation is very often the dissociation of the metal–ligand bond. This process has been widely used for the elimination of CO, dienes, phosphines, and other ligands. The primary species is usually a coordinatively unsaturated compound in which the metal has not undergone a change of its oxidation state [Eq. (17)]. This free coordination site can be occupied either by (a) addition of a new ligand with retention of the oxidation state [(Eq. (18)] or (b) addition with increase of the oxidation state of the metal. This reaction is termed oxidative addition [Eq. (19)]. Although the mechanism of process a appears to be well understood, the details of mechanism b are a matter of current discussion (*324*, *345*, *249*, *424*). In the oxidative addition reaction a formal transfer of two electrons from the metal to the ligand occurs, often resulting in the cleavage of an intraligand bond. Many reactions involving oxidative addition are, therefore, combined with transformation of ligands. The reverse of an oxidative addition reaction is called reductive elimination [Eq. (20)].

$$\mathrm{M(0)L}_n \xrightarrow{h\nu} \mathrm{M(0)L}_{n-1} + \mathrm{L} \qquad (17)$$

$$\mathrm{M(0)L}_{n-1} + \mathrm{L'} \longrightarrow \mathrm{M(0)L}_{n-1}\mathrm{L'} \qquad (18)$$



$$\mathrm{M(0)L}_{n-1} + \mathrm{XY} \longrightarrow \mathrm{L}_{n-1}\mathrm{M(II)}\begin{smallmatrix}\diagup\mathrm{X}\\ \diagdown\mathrm{Y}\end{smallmatrix} \qquad (19)$$



$$\mathrm{L}_{n-1}\mathrm{M(II)}\begin{smallmatrix}\diagup\mathrm{X}\\ \diagdown\mathrm{Y}\end{smallmatrix} \longrightarrow \mathrm{L}_{n-1}\mathrm{M(0)} + \mathrm{XY} \qquad (20)$$

1. Substitution of CO *in Simple Metal Carbonyls*

The principal process on irradiation of metal carbonyls is the substitution of CO by other ligands such as *n* donors (phosphines, amines) or π donors (olefins, dienes). Most of these reactions occur by dissociative activation (S_N1): CO is eliminated from the excited molecule and the ligand L adds to the coordinatively unsaturated species (*332*):

$$\mathrm{M(CO)}_n \xrightarrow{h\nu} [\mathrm{M(CO)}_n]^* \longrightarrow \mathrm{M(CO)}_{n-1} + \mathrm{CO}$$
$$\mathrm{M(CO)}_{n-1} + \mathrm{L} \longrightarrow \mathrm{M(CO)}_{n-1}\mathrm{L}$$

The quantum yield of the dissociative process for $\mathrm{M(CO)_6}$ (M = Cr, Mo, W) was found by Strohmeier *et al.* (*545*) to be one independent of the solvent or the wavelength of excitation. The unit efficiency of this process has been questioned (*318*) because inner light-filter action of the products may have limited the accuracy of the measurement. This is a general problem for quantum yield determinations whenever the degree of conversion is so high that the products absorb a significant amount of light. The interested reader is referred to a recent paper containing a rate expression for consecutive first-order (photochemical) reactions

$$A \xrightarrow{h\nu} B \xrightarrow{h\nu} C$$

which takes account of the absorptions of B and C (*375*).

Substitution of CO in metal carbonyl compounds by associative (S_N2) activation seems to be an unusual occurrence. A detailed study of the reaction,

$$MnNO(CO)_4 + L \xrightarrow{h\nu} MnNO(CO)_3L + CO \tag{21}$$

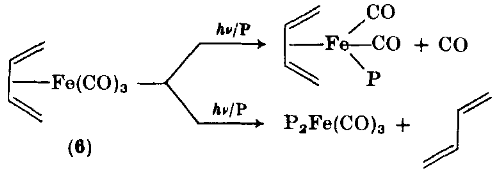
revealed that the quantum yield is dependent on the concentration of L if $L = PPh_3$, but not when $L = AsPh_3$ (*297*) [Eq. (21)]. It is suggested that the reaction with the weaker nucleophile $AsPh_3$ proceeds via an S_N1 mechanism, whereas in the case of PPh_3 an associative activation also occurs.

2. *Wavelength-Dependent Substitution Reactions of Metal Carbonyl Derivatives*

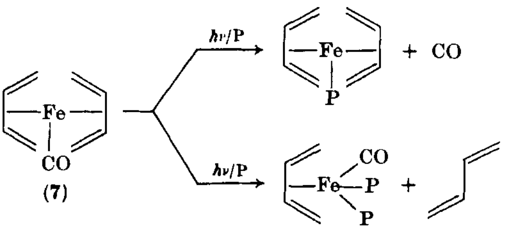
Photolysis of substituted metal carbonyls causes substitution not only of CO but also of other ligands:

$$\begin{tikzcd} & M(CO)_{n-2}LL' + CO \\ M(CO)_{n-1}L \arrow[ur, "h\nu/L'"] \arrow[dr] & \\ & M(CO)_{n-1}L' + L \end{tikzcd}$$

In several cases the ratio of the quantum yields of these two processes changes with the wavelength of excitation (Table VII). A well-studied example of such wavelength-dependent photosubstitution is the reaction of diene–iron carbonyl complexes with phosphines (P) (*315, 316*):



(6)



(7)

Although CO substitution predominates upon irradiation at short wavelengths, the diene substitution becomes more important at longer wavelengths (Table VII).

The possibility of influencing the course of reaction by varying the excitational energy offers interesting preparative applications, for instance in the synthesis of bis(butadiene)trimethylphosphiteiron. This complex is only obtained in a satisfactory way using 254-nm irradiation.

There have been several attempts at explaining such wavelength-dependent reactions (see Section III, A) (*615*, *629*, *630*, *631*, *599*). Of the models developed to predict the course of reaction, we will discuss that of Wrighton, which is based on simple ligand field considerations (*610*). The pattern of *d*-orbital splitting of a $M(CO)_5L$ complex with C_{4v} structure (e.g., M = Mo, W; L = NH_3, piperidine) is shown in Fig. 7 (Section III, D). The six *d* electrons occupy the d_{xy}, d_{xz}, and d_{yz} orbitals. From this scheme two types of one-electron excitation can be derived. The lowest-energy excitation results in population of the d_{z^2} orbital causing labilization along the *z* axis (OC—M—L), leading to preferential cleavage of the M—L bond. Labilization along the *x* and *y* axes, due to population of the $d_{x^2-y^2}$ orbital is achieved by higher-energy excitation and is expected to cause loss of equatorial CO. Photosubstitution experiments on $M(CO)_5L$ (M = Mo, W; L = NH_3, *n*-propylamine, piperidine) are consistent with this model (*610*). Irradiation in the long-wavelength region yields efficient substitution of L, whereas at shorter wavelength CO substitution increases. The additional L substitution occurring upon high-energy excitation is explained by competitive internal conversion to the lower-excited state (compare Fig. 1, Section II).

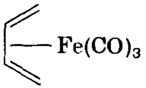
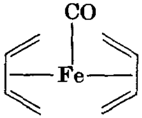
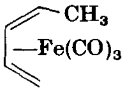
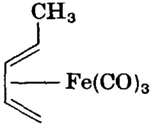
Analogous behavior was shown by $W(CO)_5L$ (L = pyridine, 2-styrylpiperidine, 4-styrylpiperidine), but in the case of styrylpiperidine isomerization of the ligand was also observed (Φ trans → cis = 0.49 at 436 nm) (*618*). The authors conclude that the lowest-excited ligand field state (labilization in direction of the *z* axes) leads either to dissociation of the W—L bond or to isomerization by electronic energy migration. Substitution of L is reduced when the isomerization begins to appear. The decrease in isomerization at short wavelengths parallels that for the photosubstitution of L.

3. *Photochemical Isomerization of Organo-Transition-Metal Complexes*

a. Cis–Trans Isomerization of Ligands. Irradiation of olefins or dienes in the presence of transition metal carbonyl compounds can

TABLE VII

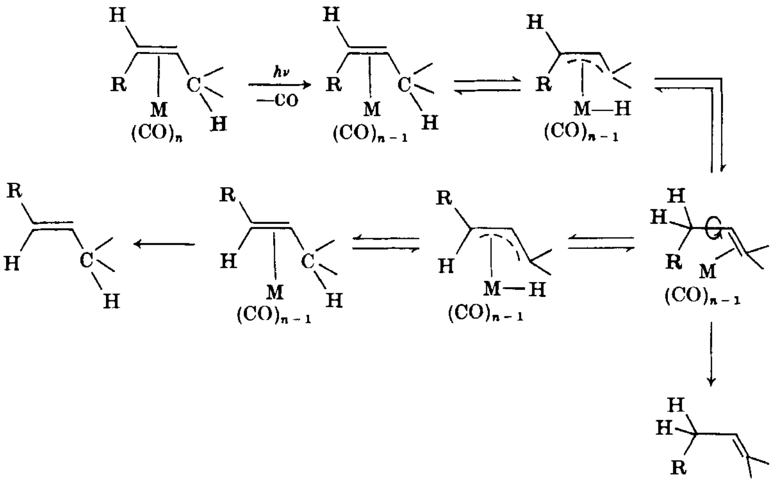
WAVELENGTH-DEPENDENT QUANTUM YIELDS FOR THE SUBSTITUTION OF CO (Φ^{CO}) AND DIENES (Φ^{D}) IN DIENE–CARBONYLIRON COMPLEXES[a]

Complex	[complex] (moles/liter)	$[P(OCH_3)_3]$ (moles/liter)	254 nm Φ^{CO}	254 nm Φ^{D}	405 nm Φ^{CO}	405 nm Φ^{D}
	1.1×10^{-2}	0.1	0.28	0.08	0.05	0.01
	5.7×10^{-3}	0.2	0.14	0.03	0.01	0.01
	9.6×10^{-3}	0.1	0.46	0.064		
	9.5×10^{-3}	0.1			0.05	0.088
	10.4×10^{-3}	0.1	0.23	0.016		
	10.2×10^{-3}	0.1			0.03	0.009

[a] Data from Kirsch *et al.* (*316*).

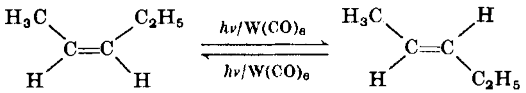
result in their cis–trans isomerization. Three different mechanisms have to be considered for this reaction.

i. Isomerization is brought about by a sequence of addition–elimination reactions, according to the so-called π-allyl-hydride mechanism (*374*, *332*), which is often accompanied by a migration of the double bond via a 1,3-hydrogen shift (Scheme 1).



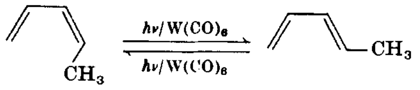
SCHEME 1

This mechanism appears to be operative in the mutual isomerization of *cis*- and *trans*-2-pentene (*622*),



(22)

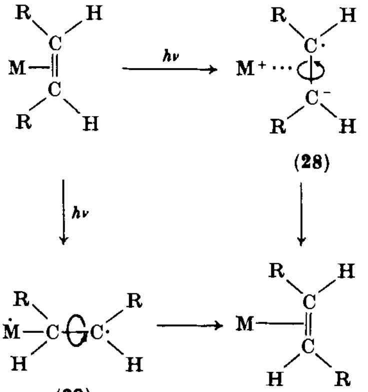
as well as in that of 1,3-pentadiene,



(23)

and 2,4-hexadiene (*617*, *622*). The action of light in this case is solely restricted to the formation of a free coordination site by photochemical cleavage of a metal–CO bond.

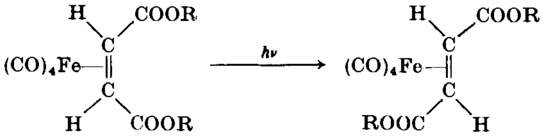
ii. In those cases where no readily abstractable β-hydrogen is available, an intermediate resulting from the electronic excitation of the metal–olefin system appears to be responsible for cis-trans isomerization. Proposals for the isomerizing species include **28** (*332*) and **29** (*622*):



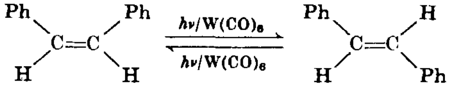
(28)

(29)

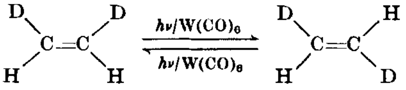
In neither species is the metal–olefin bond completely dissociated; however, in both cases facile rotation around the C—C bond is possible. Examples for this type of mechanism are



(*492*)



(*616*)

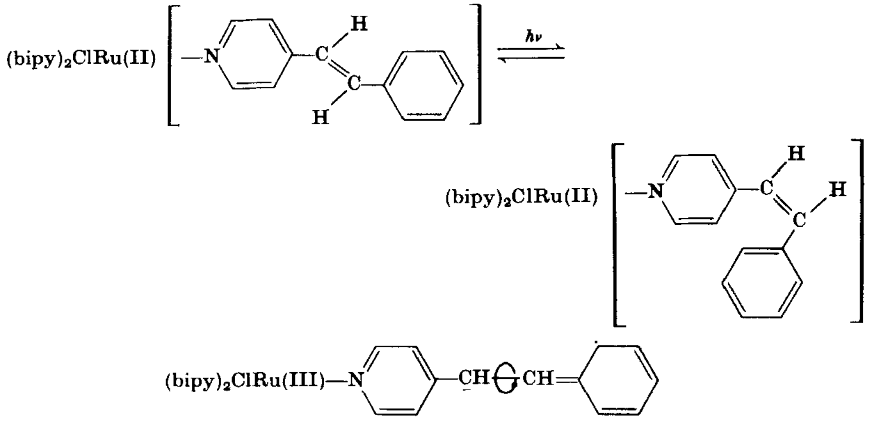


(*622*)

Only in the first case have the complexes of the *cis*- and *trans*-olefin been isolated (*492*).

iii. Cis-trans isomerization of a ligand double bond not directly coordinated to the metal may result from excitation of a charge-transfer transition (e.g., CTML), by excitation of an intraligand transition, or by energy transfer (see Section III, E for the latter case).

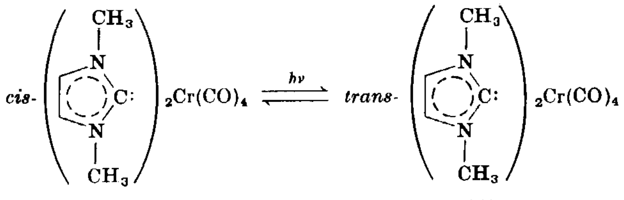
The best-studied example for ligand isomerization by CTML excitation is the cis-trans isomerization of the stilbazole ligand in $[Ru(2,2'\text{-bipy})_2(\textit{cis}\text{-4-stilbazole})_2]^{2+}$ and $[Ru(2,2'\text{-bipy})_2(\textit{cis}\text{-4-stilbazole})Cl]^{+}$ (*627*, *628*):



(30)

Investigation of the wavelength dependence of the isomerization pointed to at least two different types of excited states. Irradiation in the long-wavelength region converted the cis complexes efficiently to the trans forms, whereas the trans complexes gave only small yields of the cis isomers. By contrast, irradiation at shorter wavelengths of the trans complexes resulted in efficient isomerization to the cis forms. The authors suggest that long-wavelength excitation results in a CTML transition (d-π^*) to a state that can be described as a metal-oxidized radical anion of the ligand (**30**) that preferentially undergoes cis-to-trans isomerization. Irradiation at shorter wavelengths produces predominantly intraligand excited states of the olefinic system (π-π^*) which decay to cis and trans isomers with nearly equal probability.

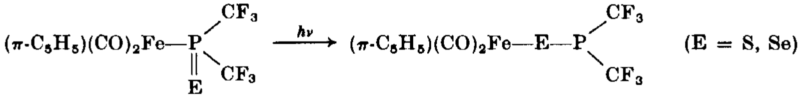
b. Positional Isomerization of Ligands. Photolysis of the bis(carbene) complexes (**31**) (M = Cr, Mo, W) results in isomerization, yielding the corresponding trans complexes (**32**) (*415*, *416*):



(31) **(32)**

Irradiation of species **31** is expected to lead to the elimination of one CO group. In the resulting coordinatively unsaturated intermediate, the large heterocyclic ligand can change to the sterically preferred trans position. The species is then stabilized by the recoordination of CO.

Linkage isomerism has also been observed (*167*, *168*):



$$(\pi\text{-}C_5H_5)(CO)_2Fe{-}\overset{\displaystyle E}{\underset{}{P}}(CF_3)_2 \xrightarrow{h\nu} (\pi\text{-}C_5H_5)(CO)_2Fe{-}E{-}P(CF_3)_2 \qquad (E = S, Se)$$

4. *Photodissociation of Metal–Metal Bonds*

The structure of the dimeric metal carbonyls $M_2(CO)_{10}$ (M = Mn, Re) can be viewed as the combination of two $M(CO)_5$ units, both having C_{4v} structures and a d^7-electron configuration (Fig. 12). The metal–metal bond is formed by interaction of the d_{z^2} orbitals of the $M(CO)_5$ moieties, which are occupied by the unpaired electrons. In Fig. 12 a simple MO scheme demonstrates this bonding situation (*609*).

The UV spectra of the $M_2(CO)_{10}$ complexes exhibit strong absorption bands [e.g., $Re_2(CO)_{10}$: $\lambda_{max} = 310$ nm, $\varepsilon = 17{,}000$], which were assigned to the σ-σ^* transition on the basis of their polarization (*367*). Excitation in this wavelength region can result in cleavage of the metal–metal bond, caused by the population of the antibonding σ^* orbital.

Kinetic studies of polymerization reactions, which were photoinitiated by $M_2(CO)_{10}$, appeared to indicate an unsymmetric cleavage of the metal carbonyl (*36*, *37*):

$$M_2(CO)_{10} \xrightarrow{h\nu} M(CO)_4 + M(CO)_6$$

By contrast, results of other authors (*248*) pointed toward a symmetric cleavage. Irradiation of $Mn_2(CO)_{10}$ ($\lambda \geq 350$ nm) in THF produced paramagnetic species, which were suggested to be $\cdot Mn(CO)_5$ on the basis of their reactions. However, in a recent study it was found

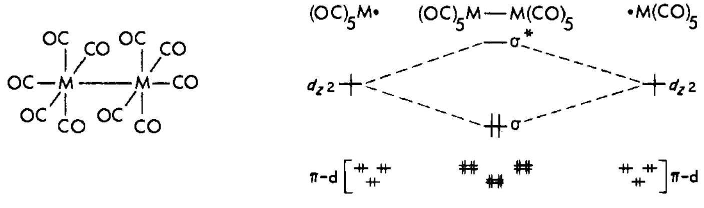


FIG. 12. Molecular orbital scheme for the metal–metal bond in $M_2(CO)_{10}$. [From Wrighton (*609*).]

that this radical species is generated only in the presence of traces of oxygen (*187*). The authors, therefore, assigned it to the peroxocomplex $\cdot O_2Mn(CO)_5$.

Storage of the irradiated solution led to quantitative recombination to $Mn_2(CO)_{10}$, whereas addition of iodine resulted in the formation of $Mn(CO)_5I$. No re-formation of $Mn_2(CO)_{10}$ could be observed when N_2 was bubbled through the irradiation solution, but the radical species eliminated CO (*248*).

Study of the photochemistry of $Re_2(CO)_{10}$ (*611*) gave further evidence for a symmetrical splitting. Irradiation in CCl_4 yielded $Re(CO)_5Cl$. The quantum yield for the appearance of $Re(CO)_5Cl$ is about twice the disappearance yield of $Re_2(CO)_{10}$. The value of 0.6 for the latter indicates that M—M bond cleavage is the major photoreaction in $Re_2(CO)_{10}$.

A detailed quantitative investigation of the photochemistry of the complexes **33**–**37** [$Mn_2(CO)_{10}$ (**33**); $Mn_2(CO)_9PPh_3$ (**34**); $Mn_2(CO)_8(PPh_3)_2$ (**35**); $Re_2(CO)_{10}$ (**36**); $MnRe(CO)_{10}$ (**37**)] was recently reported (*613*). Some of the results are briefly summarized.

Photolysis of **33**–**37** in CCl_4 ($\lambda \geqslant 366$ nm) yielded the corresponding mononuclear metal carbonyl chlorides ($\Phi = 0.5$). Irradiation of **33**, **36**, or **37** in the presence of I_2 resulted in nearly quantitative formation of $M(CO)_5I$ species. A mixture of **33** and **36** yielded **37** on irradiation. Flash photolysis of **37** and **34** occurred according to

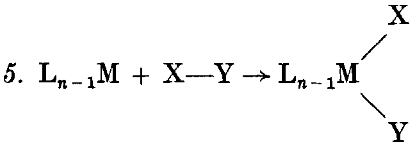
$$MnRe(CO)_{10} \xrightarrow{h\nu} Mn_2(CO)_{10} + Re_2(CO)_{10} \quad (\sim 1{:}1) \tag{24}$$

$$Mn_2(CO)_9PPh_3 \xrightarrow{h\nu} Mn_2(CO)_{10} + Mn_2(CO)_8(PPh_3)_2 \quad (\sim 1{:}1) \tag{25}$$

These reactions are interesting "preparative" applications of high-intensity photochemistry, using flash techniques. All the observed photochemistry can be interpreted as arising from homolytic metal–metal bond cleavage.

The mechanism of the formation of products resulting from CO substitution (*420*) (e.g., **34** from **33**) is still a matter of discussion (*609*). In contrast to the direct photochemical cleavage of a M—CO bond in $M_2(CO)_{10}$ (*420*), a recent proposal by Wrighton suggests that metal–metal bond cleavage precedes the loss of CO:

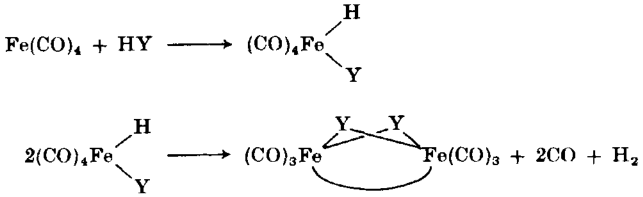
$$\begin{tikzcd}
M_2(CO)_{10} \arrow[r, shift left, "h\nu"] & 2M(CO)_5 \arrow[l, shift left] \arrow[r, "L"] & M(CO)_4L + CO \arrow[d, "M(CO)_5"] \\
 & & (CO)_5M\text{—}M(CO)_4L
\end{tikzcd}$$



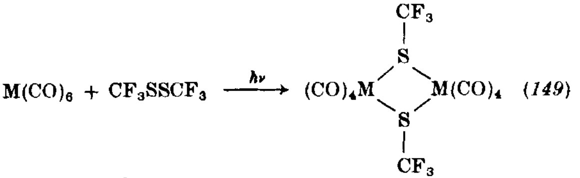
$$5.\ L_{n-1}M + X{-}Y \rightarrow L_{n-1}M\begin{matrix}X\\ \\ Y\end{matrix}$$

The coordinatively unsaturated species $L_{n-1}M$, which is produced by photodissociation of ML_n, can add to covalent molecules X—Y by cleavage of the X—Y bond (oxidative addition).

a. X = H. Reaction of $Fe(CO)_4$ with HBr or HI yielded the hitherto unknown dimeric halogen iron tricarbonyls $[Fe(CO)_3Y]_2$ (Y = Br, I) (*337*):



b. X—Y = RSSR.



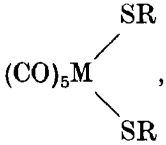
(*149*) (26)

(M = Mo, W)

$$[(\pi\text{-cp})M(CO)_3]_2 + CF_3SSCF_3 \xrightarrow{h\nu} [(\pi\text{-cp})M(CO)_3SCF_3]\ (\mathit{150}) \qquad (27)$$

(M = Mo, W)

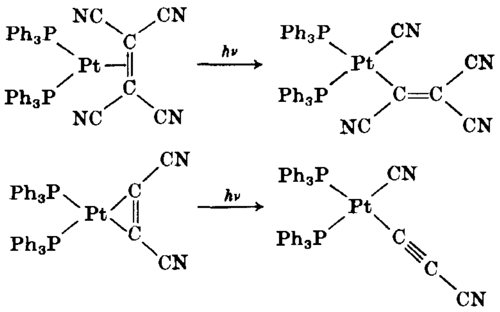
The classification of reactions (26) and (27) as oxidative addition reactions is not clear-cut. However, the reviewers surmize that the first step in Eq. (26) is the oxidative addition of RSSR to $M(CO)_5$, giving



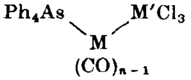
$$(CO)_5M\begin{matrix}SR\\ \\ SR\end{matrix}$$

, from which the final product originates.

c. X—Y = R—*Halogen*. An example for this reaction, the photolysis of 1,2-dihaloethylene tetracarbonyliron complexes, has already been discussed in Section III, A (*236*). For X—Y = R—pseudohalogen, similar reactions occur (*22, 560*):



d. X—Y = M—M′. Irradiation of $Ph_4As—M'Cl_3$ (M′ = Ge, Sn) in the presence of $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, or $Fe(CO)_5$ yielded **38** (*479*).



(M = Cr, Mo, W, Fe)

(**38**)

The formation of **38** can be considered as the oxidative addition of an As—M′ bond to $M(CO)_{n-1}$, as well as insertion of $M(CO)_{n-1}$ into the As—M′ bond. Because the transition metal is the subject of this article, the former classification is relevant.

6. *Insertion and Elimination Reactions*

Wojcicki (*607*) suggested the following definition of insertion reactions of organometallic compounds:

$$M—X + Y \longrightarrow M—Y—X$$

where M is a metal, and X and Y are monoatomic or polyatomic species.

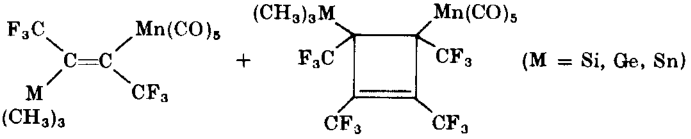
This type of reaction may be considered as a special case of addition of M—X to the substrate Y, involving cleavage of the M—X bond. Very often this reaction is reversible; the extrusion of Y is called elimination.

Insertion reactions may be classified in two ways (*607*): (a) according to the nature of the entering ligand (e.g., CO, SO_2, SO_3, S, organic isocyanides) or (b) according to the nature of the M—X linkage, which is engaged in the reaction. We will follow the last suggestion.

a. M—X = M—M′. The behavior of various fluoroalkenes and alkynes toward $(CH_3)_3M—Mn(CO)_5$ was studied by Clark *et al.* (*115*).

$$(CH_3)_3Si—Mn(CO)_5 + CF_2{=}CF_2 \xrightarrow{h\nu} (CH_3)_3Si—CF_2—CF_2—Mn(CO)_5$$

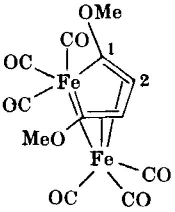
$$(CH_3)_3M—Mn(CO)_5 + CF_3—CF{=}CF—CF_3 \xrightarrow{h\nu}$$



(39)

Besides the products of insertion into the M—M′ bond, they also observed secondary products, e.g. **39**.

b. M—X = M—C. Photolysis of **40** in the presence of diphenyldiazomethane yielded complex **41** (*23*). The formation of **41** can result from insertion of diphenylcarbene into the Fe—C_1 bond, rupture of the newly formed Fe—C bond, rotation about C_1—C_2, and subsequent coordination of the oxygen to iron.



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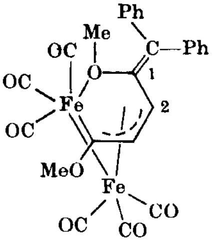
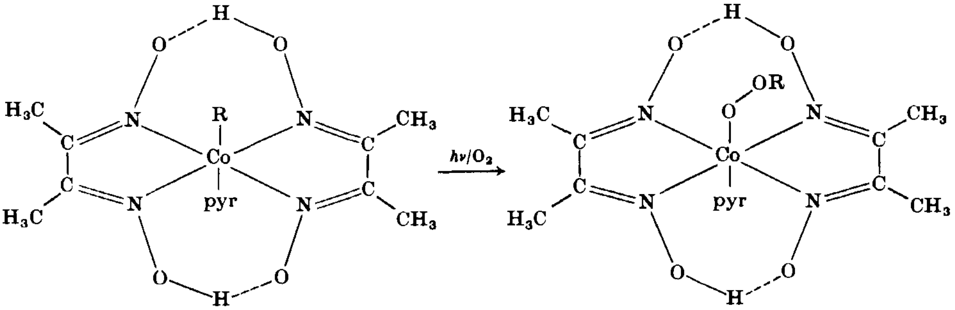


(41)

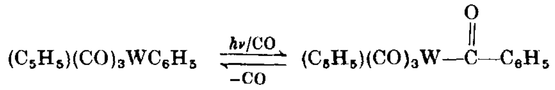
In recent years Giannotti *et al.* (*216*, *221*, *205*) have studied the photochemical insertion of O_2 into the Co–carbon bond of a series of cobaloximes (**42**), giving the stable peroxo compounds (**43**):



(42) **(43)**

This reaction is discussed in more detail in Section V, E.

Several examples for photochemical insertion of CO in metal–carbon bonds (carbonylation reaction) have been reported (*607*), for instance (*402*):



$$(C_5H_5)(CO)_3WC_6H_5 \underset{-CO}{\overset{h\nu/CO}{\rightleftharpoons}} (C_5H_5)(CO)_3W{-}\overset{\overset{O}{\|}}{C}{-}C_6H_5$$

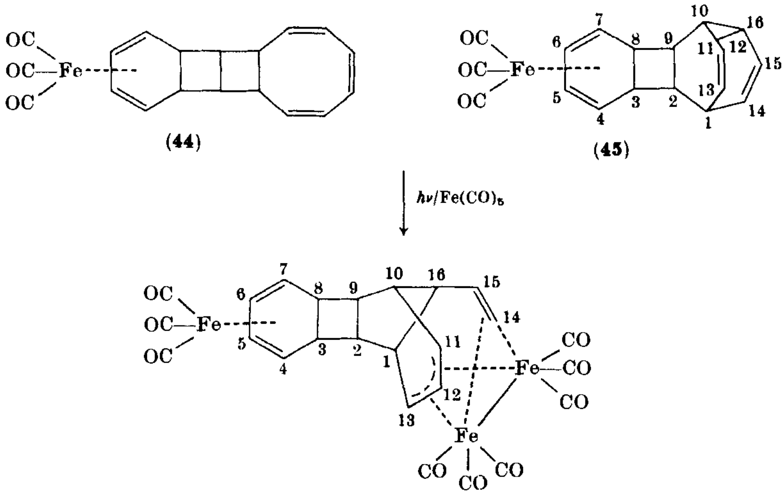
Carbonylation reactions often occur with concomitant skeletal rearrangement (see following). Several examples of decarbonylation will be discussed in detail in Section IV, B, which also contains some remarks on the mechanism of this reaction. For a survey of carbonylation and decarbonylation reactions, see Ref. *607*.

c. M—X = M—H.

$$(CH_3)_3SiOs(CO)_4H \xrightarrow{h\nu/C_2F_4} (CH_3)_3SiOs(CO)_4(C_2F_4H) \quad (\mathit{321})$$

7. *Skeletal Rearrangements*

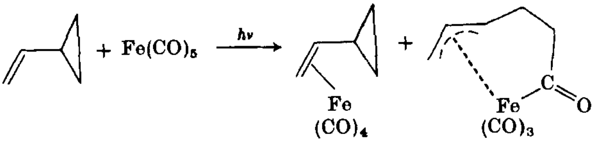
Light-induced reaction of the iron–tricarbonyl complexes (**44** and **45**), formed from cyclooctatetraene dimers (*463*), afforded **46** as shown by X-ray analysis (*591*). In the conversion of **44** to **46**, a vinyl-substituted six-membered ring has been formed from an eight-membered ring.



(**44**) (**45**)

(**46**)

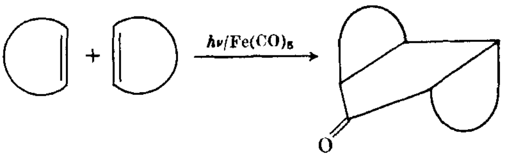
Photoinduced insertion of CO into metal–carbon bonds can accompany skeletal rearrangements. For example the photoreaction of vinylcyclopropane with $Fe(CO)_5$ yielded **47** and **48** (*20*):



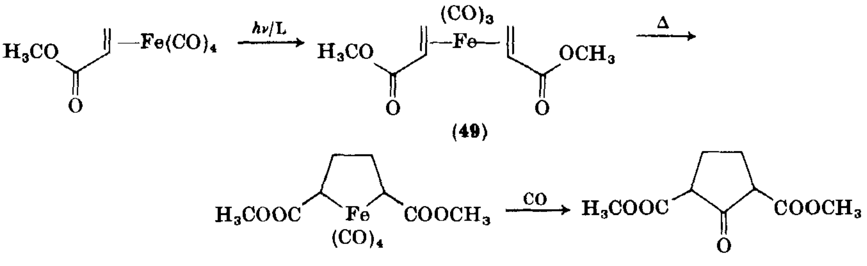
(**47**) (**48**)

8. C—C *Bond Formation*

A detailed study of photochemically induced C—C bond formation between two olefins with subsequent CO insertion, yielding cyclopentanone derivatives has been published (*373*, *372*):



Insight into the mechanism of this reaction has been obtained by irradiation of $Fe(CO)_4L$ in the presence of L (L = methylacrylate). At room temperature, a ferracyclopentane (**50**) is formed whose reaction with CO yields the cyclopentanone derivative (**51**) (*237*):

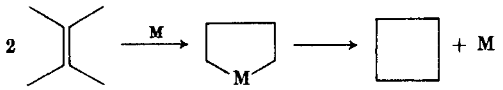


(**49**) (**50**) (**51**)

($L = CH_2{=}CH{-}COOCH_3$)

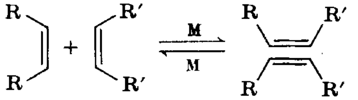
By performing the reaction at low temperature (−30°C), the hitherto unknown bis(olefin)tricarbonyliron (**49**) has been isolated and shown to be an intermediate in this reaction.

Evidence is accumulating that the transition metal-catalyzed formation of cyclobutanes from 2 olefin molecules occurs via metallacyclopentanes as intermediates (*253*):



(M = transition metal)

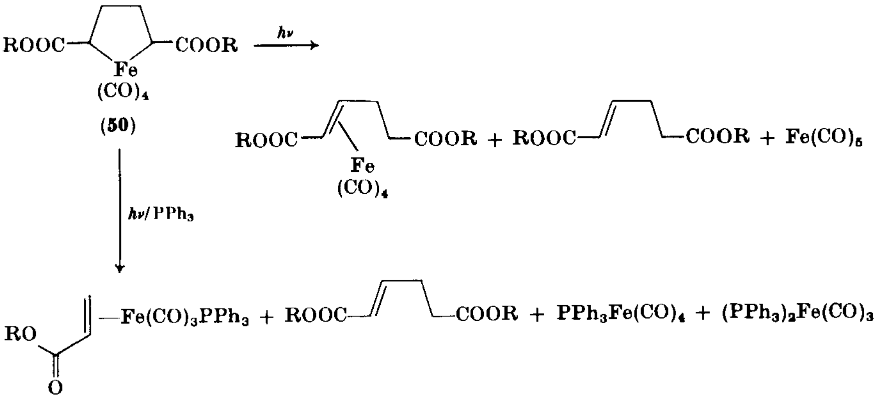
Much mechanistic work has, therefore, been directed toward the synthesis and reactions of metallacyclopentanes. Compounds of this type have also been discussed as intermediates in metathesis reactions (*239*).



9. M—C *Bond Cleavage*

The involvement of metallacyclopentanes as intermediates in the formation of cyclobutanes and in metathesis reactions, as discussed above, makes their photochemistry interesting.

An investigation of the photoreactions of **50** gave the following results (*238*):

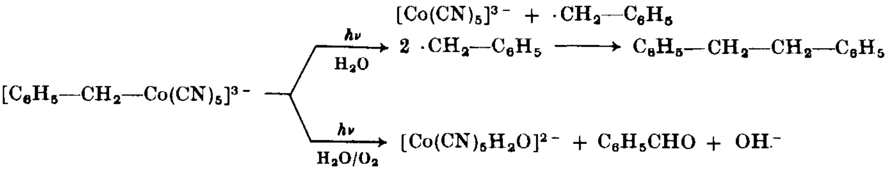


The understanding of the mechanistic details of this reaction will require more knowledge about the photochemical cleavage of transition metal–carbon single bonds. The photochemical formation of radicals from nontransition organometallic compounds, e.g., mercury alkyls, is a well-known reaction (*44*, *119*):

$$\mathrm{R{-}Hg{-}R} \xrightarrow{h\nu} \mathrm{R{-}Hg}\cdot + \mathrm{R}\cdot$$

The corresponding reaction with transition metal alkyls is restricted to a few examples, especially to alkylcobalt complexes (see Sections V, D and E).

Irradiation of aqueous $[C_6H_5—CH_2—Co(CN)_5]^{3-}$ in the CTLM (benzyl → Co) transition resulted in a redox reaction yielding $Co(CN)_5{}^{3-}$ and dibenzyl (from benzyl radicals). If this reaction was carried out in the presence of oxygen, no $Co(CN)_5{}^{3-}$ was observed and the benzyl radicals were oxidized to benzaldehyde (*585*):

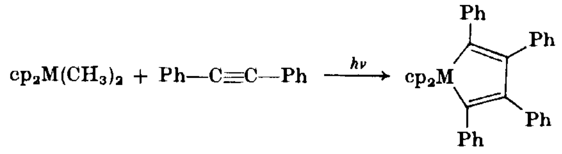


Recently, the photochemical reaction of dimethylderivatives of titanocene, zirconocene, and hafnocene have been reported (*11*). Irradiation resulted in a homolytic cleavage of the methyl–metal bond, by which the metal is reduced to a lower oxidation state:

$$(C_5H_5)_2M(CH_3)_2 \xrightarrow{h\nu} (C_5H_5)M + 2\ \cdot CH_3$$
$$(M = Ti, Zr, Hf)$$

The methyl radicals undergo further reactions (e.g., methane formation).

When photolysis is carried out in the presence of acetylenes, metallacycles are the major products:



(M = Ti, Zr, Hf)

10. *Photocatalysis*

It is difficult to give a concise definition of the term photocatalysis. In an organometallic catalytic photoreaction, a catalyst, which is formed and (or) activated photochemically *in situ*, brings about the thermal conversion of more than 1 substrate molecule (per catalyst molecule). Depending on the quantum yield of catalyst formation (or activation), the total turnover (T) of substrate can be less than ($\Phi_T \leqslant 1$) or more than ($\Phi_T > 1$) 1 molecule per photon absorbed.

Wrighton (*614*) has suggested that the term photocatalysis be reserved for the case of $\Phi_T > 1$. He also writes: "We find, empirically, that continuous photolysis accelerates many photocatalytic reactions, and in many cases we find no measurable substrate transformation without continuous photolysis. The term *photoassisted* is reserved for substrate transformations that appear to proceed according to

$$\text{metal complex} \xrightarrow{h\nu} [\text{catalyst}] \tag{28}$$

$$\text{metal complex} + \text{substrate} \xrightarrow{\Delta} \text{no reaction} \tag{29}$$

$$[\text{catalyst}] + \text{substrate} \xrightarrow{\Delta} \text{transformed substrate} + [\text{catalyst}] \tag{30}$$

$$[\text{catalyst}] \xrightarrow{\Delta} \text{poisoning} \tag{31}$$

but which require continuous photolysis" (*614*).

The reviewers would like to suggest the term *photoassisted catalytic reactions* for the general case of $\Phi_T \leqslant 1$. A determination of the quantum yield of transformed substrate provides an experimental criterion to distinguish the two kinds of catalytic reactions.

In many photoassisted catalytic reactions, light is not only required for the production of a catalyst but also for its activation and/or reactivation according to the modified (*614*) Michaelis-Menten mechanism (*232*):

$$[\text{catalyst}] + \text{substrate} \xrightleftharpoons{\Delta \text{ or } h\nu} [\text{catalyst} \cdots \text{substrate}] \tag{32}$$

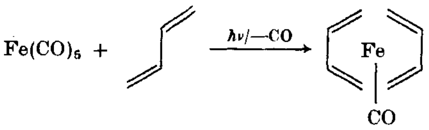
$$[\text{catalyst} \cdots \text{substrate}] \xrightarrow{\Delta \text{ or } h\nu} [\text{catalyst} \cdots \text{transformed substrate}] \tag{33}$$

$$[\text{catalyst} \cdots \text{transformed substrate}] \xrightarrow{\Delta \text{ or } h\nu} [\text{catalyst}] + \text{transformed substrate} \tag{34}$$

In such cases $\Phi_T < 1$ can be easily rationalized.

The possibility of preparing catalysts photochemically (especially at low temperatures) outside of the system undergoing the catalytic reaction, may indicate which of the steps of Eqs. (28)–(34) require light. A few examples should illustrate these principles.

a. Photochemical Production of a Catalyst (*Outside of the System To Be Catalyzed*). Irradiation of $Fe(CO)_5$ in the presence of excess butadiene leads, by substitution of four CO groups, to bis(butadiene)monocarbonyliron (**7**) (*327*, *340*) in excellent yield:

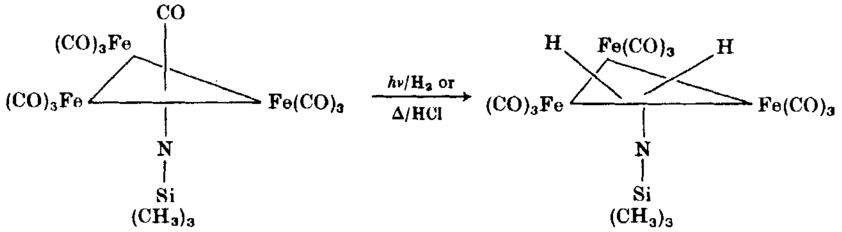


(**7**)

In the presence of PPh_3, **7** acts in the dark as a catalyst for the oligomerization of butadiene to give 4-vinylcyclohexene and 1,5-cyclooctadiene. **7** also brings about the mixed oligomerization of acrylate and dienes to give heptadienoic esters (*92*) (see Section IV, B). In these two catalytic reactions, only Eq. (28) requires light.

The cluster compound (**53**), which is formed either thermally by reaction of the corresponding carbonyl-bridged complex (**52**) (*341*) with

HCl, or by its photochemical reaction in the presence of H_2, serves as a catalyst for the photohydrogenation of olefins or dienes (*330*):



(52) **(53)**

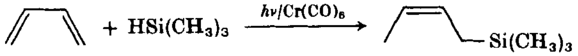
b. Photocatalytic Reactions. The hydrogenation of methylacrylate, cyclobutene, cyclobutene-3,4-dimethylycarboxylate, and 2,3-dimethylbutadiene with H_2 and **53** as a catalyst, require light for Eq. (32). Actually, one CO has to be eliminated photochemically to allow the formation of the catalyst–substrate complex. This was demonstrated by the formation of the corresponding (stable) $P(OCH_3)_3$ complex, when the photoreaction was carried out in the presence of $P(OCH_3)_3$ (*330*).

After the photochemical activation [Eq. (32)] of **53**, catalytic hydrogenation of the unsaturated substrates occurs in the dark, giving direct evidence for $\Phi_T > 1$.

According to recent evidence, the photohydrogenation of dienes with $Cr(CO)_6/H_2$ (*625, 614, 395, 507, 435, 436, 439, 437, 624*) also belongs to the group of truly photocatalytic reactions. 1,3-Diene–tetracarbonylchromium complexes, which are catalysts of this reaction, have recently been prepared (e.g., by low-temperature photolysis) and tested (*328, 339*).

Norbornadiene–$Cr(CO)_4$ is also an efficient catalyst in the photohydrogenation of dienes (*435, 436, 439, 437*). Also, $IrCl(CO)(PPh_3)_2$ has been employed as catalyst in the photohydrogenation of olefins (*547*).

Another example in which light is needed for the formation of a catalytically active species is the 1,4-hydrosilation of 1,3-dienes in the presence of $Cr(CO)_6$ (*626*):



(35)

In some cases the resulting allylsilanes are obtained in almost quantitative yields.

c. Photoassisted Catalytic Reactions. Many catalytic photoisomerization and -dimerization reactions appear to belong in this group; however, detailed quantum yield studies are missing in most cases. Table VIII provides a survey of such reactions.

d. Photoinitiation of Free-Radical Polymerization by Transition Metal Derivatives. A special case of organometallic photocatalysis is the initiation of free-radical polymerization (*29*). Many of these reactions are based on metal carbonyl photolysis. Three initiation mechanisms are commonly considered (*29*, *35*).

i. Formation of radicals from organic halides (*36*, *33*):

$$\mathrm{M(CO)}_n \xrightarrow{h\nu} \mathrm{M(CO)}_{n-1} + \mathrm{CO}$$

$$\mathrm{M(CO)}_{n-1} + \mathrm{RX} \xrightarrow[\text{addition}]{\text{oxidative}} \mathrm{R}\cdot + [\mathrm{XM(CO)}_{n-1}]$$

ii. Formation of radicals by hydrogen abstraction from C—H bonds (*34*):

$$\mathrm{M(CO)}_n \xrightarrow{h\nu} \mathrm{M(CO)}_{n-1}$$

$$\mathrm{M(CO)}_{n-1} + \mathrm{R'{-}H} \xrightarrow[\text{addition}]{\text{oxidative}} \mathrm{R'}\cdot + [\mathrm{HM(CO)}_{n-1}]$$

iii. Formation of radicals by metal–metal bond cleavage and addition of $CF_2{=}CF_2$ (*35*):

$$\mathrm{M_2(CO)}_{2n} \xrightarrow{h\nu} 2\ \cdot\mathrm{M(CO)}_n$$

$$\cdot\mathrm{M(CO)}_n + \mathrm{CF_2{=}CF_2} \longrightarrow \mathrm{(CO)}_n\mathrm{M{-}CF_2{-}CF_2}\cdot$$

The radicals formed according to processes i–iii can polymerize a variety of vinyl monomers (*36*, *32*, *29*) and olefinic substrates (*17*, *30*, *35*). Much work has been done to elucidate the primary processes in these systems (*31*, *32*, *37*, *33*, *36*); some of the complications with $Mn_2(CO)_{10}$ have already been discussed (Section IV, A 4). The detailed mechanism of radical formation by oxidative addition is still under discussion (see Section IV, A). In some cases formation of X—M—R may precede radical production. It has been suggested, that addition of a vinyl monomer to X—M—R could initiate a (non-free-radical) Ziegler-type of polymerization (*332*).

The polymerization of ethylene oxide with $Mn_2(CO)_{10}$ as a starter (*549*, *548*) and of styrene with tetrabenzylzirconium (*24*) are further examples of this application of organometallic photochemistry.

B. Discussion of Some Selected Examples

In the following section we will discuss some examples selected to give some idea of the scope and versatility of preparative applications

TABLE VIII
PHOTOASSISTED CATALYTIC REACTIONS

Reaction	Substrate	Catalyst	Ref.
Isomerization	$C_2H_2D_2$	$W(CO)_6$	*622*
	Pentenes	$W(CO)_6$ or $Mo(CO)_6$	*622*
	Hexenes	$W(CO)_6$	*622*
	Pentadienes	$W(CO)_6$ or $Mo(CO)_6$	*617*
	Hexadienes	$W(CO)_6$	*617*
	Stilbenes	$W(CO)_6$ or $Mo(CO)_6$	*616*
	N-Allylamide	$Fe(CO)_5$	*270*
	Allyl ethers	$Fe(CO)_5$	*268*
	N-Allylcarbamate	$Fe(CO)_5$	*269*
	O-Phenylcarbamate	$Fe(CO)_5$	*269*
	N-Propenylcarbamate	$Fe(CO)_5$	*269*
	1-Heptene	$IrClCO(PPh_3)_2$	*546*
		$RhHCO(PPh_3)_3$	*546*
Dimerization	Norbornadiene	$Cr(CO)_6$	*281, 263*
		$(C_6H_6)Cr(CO)_3$	*263*
		$Ni(CO)_4$	*582, 263*
		$(PPh_3)_2Ni(CO)_2$, $Co(CO)_3NO$, $(Ph_3P)Co(CO)_2NO$, $(Ph_3P)CoCONO$, $Fe(CO)_2(NO)_2$, $(Ph_3P)FeCO(NO)_2$, $(Ph_3P)_2Fe(NO)_2$, 1,4-diphenyl-1,3-butadiene-$Fe(CO)_3$	*263*

of organometallic photochemistry. The ordering of these reactions reflects principles discussed in the preceding Section IV, A.

Substitution of CO *in metal carbonyls* plays a key role in the synthesis of transition metal complexes. Irradiation of $Cr(CO)_6$ in the presence of NO yielded $Cr(NO)_4$, the final member of the so-called pseudocarbonylnickel series, $Ni(CO)_4$, $Co(CO)_3(NO)$, $Fe(CO)_2(NO)_2$, $Mn(CO)(NO)_3$, $Cr(NO)_4$ (*259, 553*).

Photosubstitution of CO in $Cr(CO)_6$ and (π-cp)$Mn(CO)_3$ by the relatively weak donor THF and subsequent addition of P_2H_4 gave the first complexes containing diphosphine as a ligand (*525*):

$$2\mathrm{Cr(CO)_6} \xrightarrow[-2\mathrm{CO}]{h\nu/\mathrm{THF}} 2\mathrm{Cr(CO)_5THF} \xrightarrow{-78^\circ,\ \mathrm{P_2H_4}} \mathrm{P_2H_4[Cr(CO)_5]_2}$$

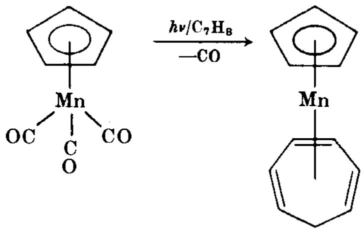
$$2(\pi\text{-cp})\mathrm{Mn(CO)_3} \xrightarrow{h\nu/\mathrm{THF}} 2(\pi\text{-cp})\mathrm{Mn(CO)_2THF} \xrightarrow{-78^\circ,\ \mathrm{P_2H_4}} \mathrm{P_2H_4}\,[(\pi\text{-cp})\mathrm{Mn(CO)_2}]_2$$

Carbene complexes of the general structure $(CO)_5MC(OR')R''$ ($M = Cr, W$; $R, R'' =$ alkyl, aryl; $R' =$ alkyl) add PR_3 at $-20°C$ to form $(CO)_5M—C(OR')R''PR_3$ by nucleophilic addition of PR_3 to the carbene carbon. Photolysis of this addition product ($M = Cr$) at $-15°C$ gave *cis*-$(CO)_4(R_3P)CrC(OCH_3)CH_3$, whereas at room temperature a mixture of the *cis*- and the *trans*-tetracarbonylchromium complex was obtained (*200*).

An interesting example for CO substitution by a π-system is reported by Herberhold *et al.* (*254*). They prepared the tetramethoxyethylene (TME) complexes $Fe(CO)_4TME$ and (π-cp)$Mn(CO)_2TME$. The CO frequencies of these complexes indicate considerably more M → TME backbonding than was expected for this "electron-rich" olefin.

The reader's attention should be drawn to the substitution of four CO groups in $Fe(CO)_5$ by dienes, leading to bis(diene)monocarbonyliron (*326, 327, 340*) (see Table X in Section IV, C); in a related reaction of dienyl tricarbonyliron salts with dienes, the (dienyl)(diene)monocarbonyliron salts are obtained, which can be reduced with hydrides to bis(diene)monocarbonyliron compounds (*16, 288*) (Table X).

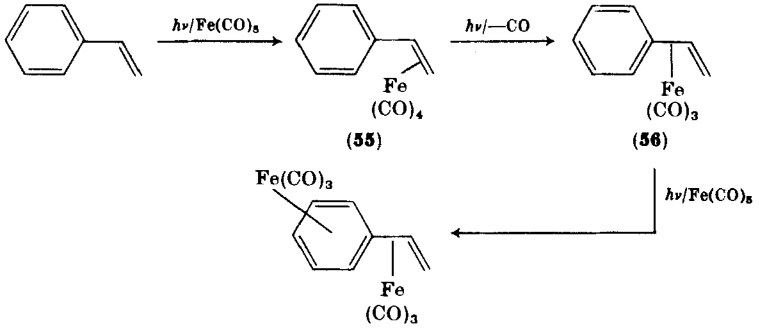
Complete photochemical substitution of CO by cycloheptatriene in cyclopentadienyltricarbonylmanganese has been reported (*423*):



(54)

The resulting complex (**54**) can easily be converted by hydride abstraction to the tropylium salt.

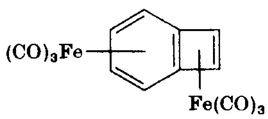
Photolysis of $Fe(CO)_5$ in the presence of styrene yielded complex (**55**) (*334*). Further irradiation leads to carbonyliron derivatives (**56**) and (**57**) where 4 or 8 electrons of the π-system are involved in coordination (*581, 577, 580, 578*):



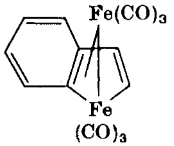
(**55**) (**56**) (**57**)

From reactions with meta-substituted styrenes, positional isomers of bistricarbonyliron complexes, corresponding to the two trapped Kékulé structures were isolated (*577*).

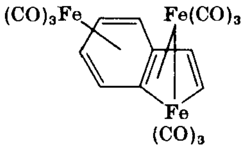
An additional example of diene-type reactivity shown by an originally aromatic system is the reaction of benzocyclobutadienetricarbonyliron with pentacarbonyliron (*575*). Besides the expected compound **58**, products **59–62**, which result from cyclobutadiene ring opening and insertion of an $Fe(CO)_3$ unit, are obtained.



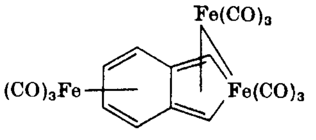
(**58**)



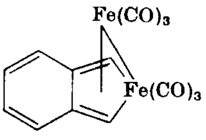
(**59**)



(**60**)

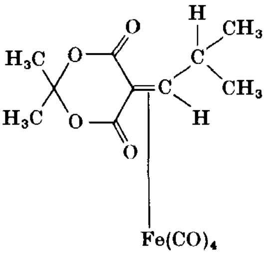


(**61**)

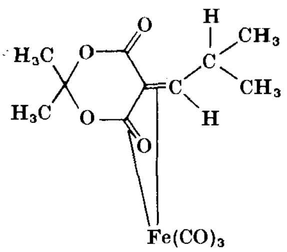


(**62**)

Photochemical synthesis of pinocarvone–, pulegone–, and benzalacetophenone–$Fe(CO)_3$ complexes have been reported (*333*). In all cases bonding to the iron involves only the π-system of the 1-oxadiene systems, and not the nonbonding electrons of the keto group. The same bonding feature was found in the $Fe(CO)_4$ (**63**) and $Fe(CO)_3$ (**64**) complexes of isobutylidene Meldrum's acid, which were prepared photochemically (*338*).

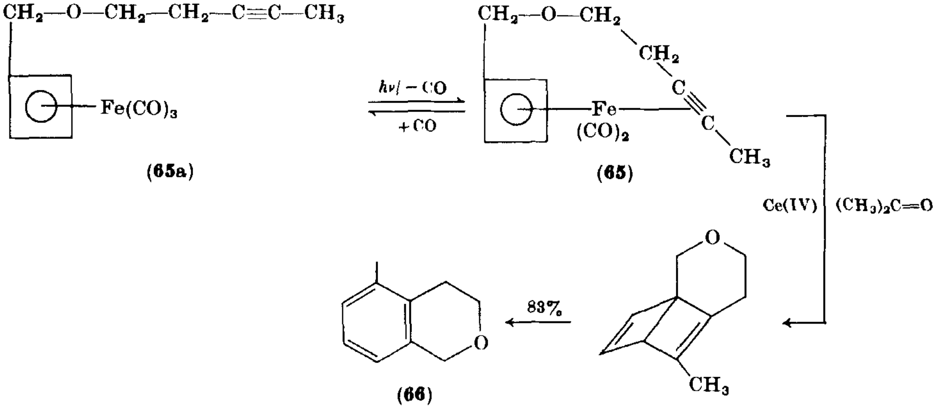


(63)



(64)

A reversible intramolecular CO substitution was suggested as the first step in the preparation of **66** via the intermediate complex **65** starting from **65a** (*240*) (Scheme 2).



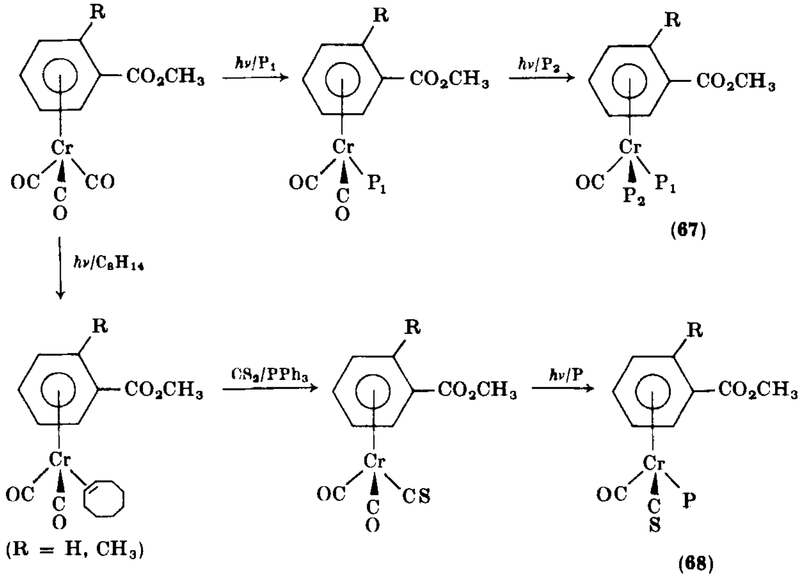
SCHEME 2

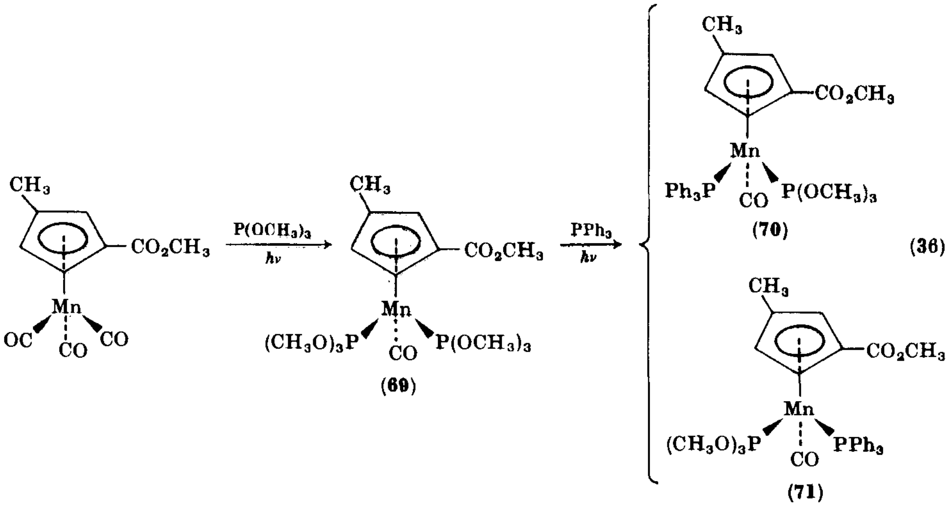
The mechanism and preparative application of arene–tricarbonylchromium complexes has recently attracted considerable attention. Although in thermal substitution reactions the aromatic ligand is always replaced, it is exclusively CO, which is substituted photochemically. The only exception was the observation by Strohmeier (*552*) that the arene can be replaced photochemically by labeled benzene. Reinvestigation, using hexadeuterobenzene and ^{13}CO revealed that this process is suppressed by CO (*225*). This suggests that arene–dicarbonylchromium is also the precursor in the exchange of the aromatic system.

A series of maleic anhydride (MA) complexes of the type $ArCr(CO)_2MA$ (Ar = substituted benzene) has been prepared photochemically (*255*). A comparison of IR and NMR data of $ArCr(CO)_3$ and

$ArCr(CO)_2MA$ indicated that π-bonded MA is a better acceptor ligand than carbon monoxide.

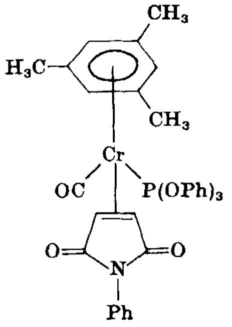
The stepwise substitution of CO by different ligands in $ArCr(CO)_3$ yielded chiral complexes due to the pseudotetrahedral configuration around the metal (*277*, *279*, *276*, *278*). The relatively easy dissociation of the Cr—P bond in complex **67** interfered with a detailed investigation; even **68** racemized in acetone.



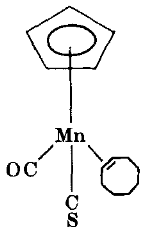


Other chiral systems have also been synthesized by photochemical substitution reactions [Eq. (36)]. The formation of the two diastereomers (**70**) and (**71**) occurs to the same extent (*366*). It is interesting to note that phosphite and not CO is substituted in the intermediate (**69**) (see also Ref. *80*).

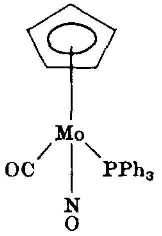
Compounds **72**–**74** are other systems with chiral metal centres that have been prepared photochemically (*394*, *186*, *185*, *379*):



(**72**)

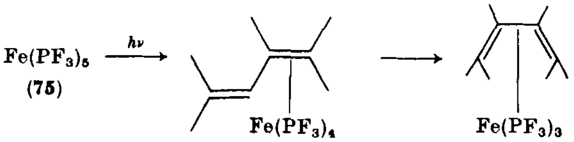


(**73**)



(**74**)

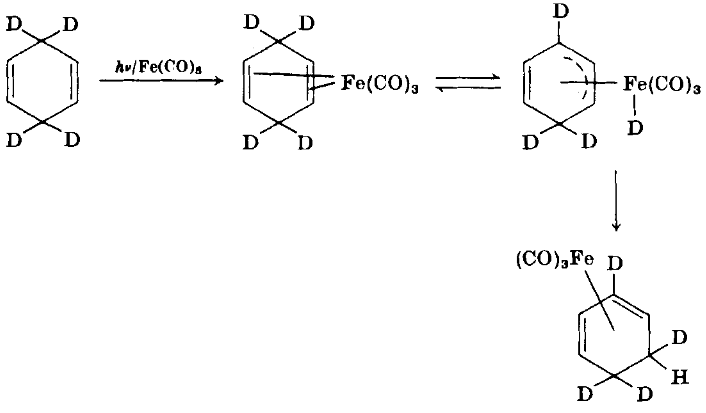
Although the photosubstitution of phosphines in phosphine–carbonylmetal complexes is an exceptional case (see, e.g., **69**) the photochemistry of pentakis(trifluorophosphine)iron has found interesting synthetic applications. Substitution by conjugated dienes yields (π-diene)tris(trifluorophosphine)iron (0) complexes (*349*, *350*):



In some cases, the monosubstituted intermediates (π-diene)Fe$(PF_3)_4$ were identified by their mass and ^1H NMR spectra. Substitution of PF_3 in (**75**) has also been achieved with various monoolefins (*347*, *348*) and with H_2 (*352*).

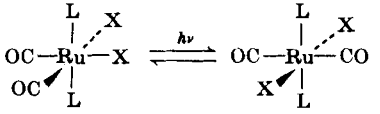
Ultraviolet irradiation of $HCo(PF_3)_4$ and a mixture of $HCo(PF_3)_4$ with $HIr(PF_3)_4$ resulted in elimination of PF_3 and formation of the bridged complexes $(PF_3)_3Co(H)(PF_2)Co(PF_3)_3$ and $(PF_3)_3Co(H)(PF_2)$-$Ir(PF_3)_3$ (*353*).

One major application of the photochemical formation of a free coordination site at a transition metal involves *isomerization reactions with hydrogen transfer via metal hydride intermediates* (see Section IV, A, 3, a). A typical example is the irradiation of $Fe(CO)_5$ in the presence of cyclohexa-1,4-dienetricarbonyliron. By labeling the methylene groups of the 1,4-diene with deuterium and analyzing the product (**76**), it was shown that the formation of the conjugated diene occurs via a π-allyl–hydridotricarbonyliron intermediate (*9*, *148*).



(**76**)

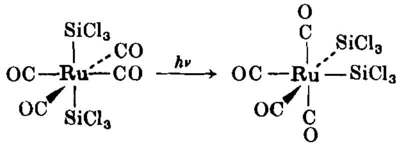
Several additional examples of *positional isomerization* should be mentioned (see also Refs. *57*, *58*, *387*,):



$$\mathrm{(OC)_2\overset{L}{\underset{L}{Ru}}X_2} \xrightleftharpoons{h\nu} \mathrm{OC{-}\overset{L}{\underset{L}{Ru}}(X)_2{-}CO}$$

(*280*)

(L = PPh$_3$; X = I)



$$\mathrm{(OC)_2\overset{SiCl_3}{\underset{SiCl_3}{Ru}}(CO)_2} \xrightarrow{h\nu} \mathrm{(OC)_2\overset{CO}{\underset{CO}{Ru}}(SiCl_3)_2}$$

(*447*)

$$cis\text{-}\mathrm{M(CO)_4I_2} \xrightarrow{h\nu} trans\text{-}\mathrm{M(CO)_4I_2} \qquad (422)$$

(M = Fe, Ru)

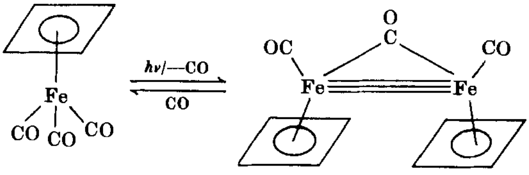
An interesting case of *photochemical cleavage of metal–metal bonds* (see also Refs. *609*, *243*, *251*) is given by the rhenium complex $[\mathrm{Re_2Cl_8}]^{2-}$ (**77**) containing a metal–metal quadruple bond (*212*). Irradiation in $\mathrm{CH_3CN}$ solution at different wavelengths (366 nm $\geqslant \lambda \geqslant$ 300 nm; λ = 254 nm) yielded $[\mathrm{ReCl_3(CH_3CN)_3}]$ (**79**). A mechanism via complex

78 has been proposed for the formation of complex **79** both on long- and short-wavelength† UV photolysis:

$$\begin{tikzcd}
\underset{(\mathbf{77})}{[Re_2Cl_8]^{2-}} \arrow[r, "h\nu(1)", "CH_3CN"'] \arrow[d, "h\nu(2)", "CH_3CN"'] & \underset{(\mathbf{78})}{[ReCl_4(CH_3CN)_2]^-} \arrow[ddl, "h\nu(2)", "CH_3CN"'] \\
\underset{(\mathbf{78})}{2[ReCl_4(CH_3CN)_2]^-} \arrow[d, "h\nu(2)", "CH_3CN"'] & \\
\underset{(\mathbf{79})}{2[ReCl_3(CH_3CN)_3]} &
\end{tikzcd}$$

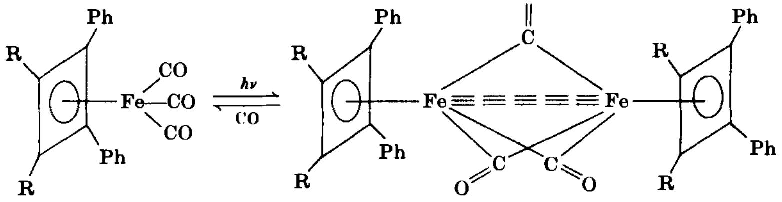
Like the cleavage of metal–metal bonds, the reverse reaction, i.e., the *formation of metal–metal bonds*, can be achieved photochemically.

Irradiation of cyclobutadiene–tricarbonyliron in THF at −40° under nitrogen resulted in formation of the dinuclear complex **80**, for which a metal–metal triple bond was proposed (*201*):



(**80**)

Analogous complexes (**81**) were obtained from the irradiation of substituted cyclobutadiene–tricarbonyliron complexes:



(R = Ph, *t*-butyl)

(**81**)

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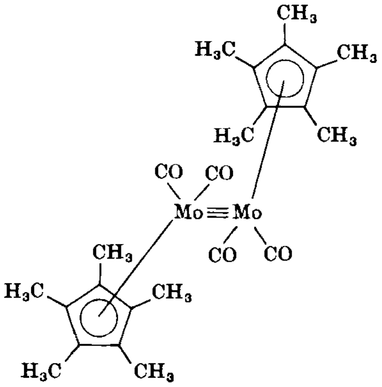
† In the proposed mechanism, $h\nu(1)$ denotes $\lambda = 254$ *nm* and $h\nu(2)$ denotes 366 nm $\geq \lambda \geq$ 300 nm.

However, all CO groups were bridging (*391*). An X-ray analysis of (**81**) (R = *t*-butyl) showed an extremely short Fe—Fe distance (2.177 Å), which is consistent with an Fe—Fe triple bond.

Irradiation of $(CH_3)_5C_5Mo(CO)_3(CH)_3$ in THF gave complex **82** of stoichiometry $[(CH_3)_5C_5Mo(CO)_2]_2$ (*307*):



(**82**)

The unsubstituted cyclopentadienyl analog $(CO)_2(\pi\text{-cp})Mo—Mo(\pi\text{-cp})(CO)_2$ was formed upon irradiation of $(CH_3)_2C{=}CH—Ge—Mo(\pi\text{-cp})(CO)_2$ (*286*; see also Ref. *178*). A survey of reactions involving metal–metal bond formation is given in Table XI (see Section IV, C).

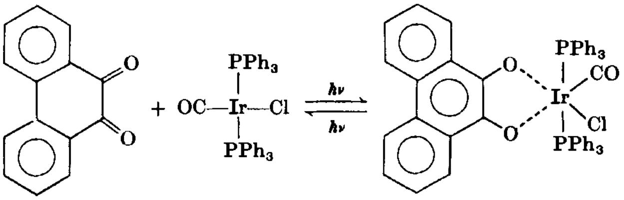
Some additional examples of *oxidative addition and reductive elimination* reactions should be mentioned to illustrate their scope and preparative importance.

Addition of R_3SiH to the coordinatively unsaturated species produced by photochemical expulsion of CO from a metal carbonyl compound provides a convenient route to the metal hydrides $L_{n-1}M(H)SiR_3$. Further reaction can lead to $L_{n-1}M(SiR_3)_2$. Reactions of this type have been carried out with R_3SiH and $Fe(CO)_5$, $C_6H_6Cr(CO)_3$, $C_5H_5Mn(CO)_3$, $C_5H_5Fe(CO)_2SiCl_3$, $C_5H_5Co(CO)_2$ (*283*, *284*), $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$ (*322*), $Os_3(CO)_{12}$ (*321*), $C_5H_5Rh(CO)_2$ (*418*), and $Re_2(CO)_{10}$ (*267*). The compound $(CH_3)_3SnH$ reacts with $Os_3(CO)_{12}$ in an analogous manner (*321*, *322*).

Binuclear complexes with R_2Si bridges result from the photoreaction of R_2SiH_2 with $W(CO)_6$ (*45*) and $Re_2(CO)_{10}$ (*266*), and of $(CH_3)_2HSi—SiH(CH_3)_2$ with $Fe(CO)_5$ (*355*).

Oxidative addition of C—H bonds to tungsten (*183*, *220*) and of B—H bonds to iron (*536*) should be mentioned in this context (see also Ref. *524*).

The oxidative addition of 9,10-phenanthrenequinone to $Ir(PPh_3)_2COCl$ can be reversed photochemically (*573*):



(37)

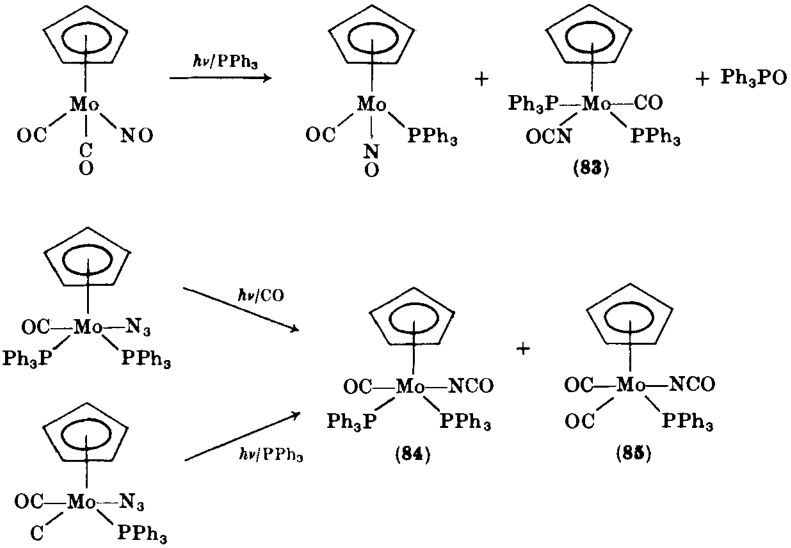
Irradiation of (π-cp)$Fe(CO)_2X$ in the presence of mercury led to insertion into the iron—X bond (*404*):

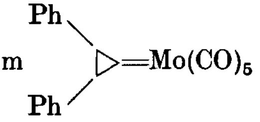
$$(\pi\text{-cp})Fe(CO)_2X + Hg \xrightarrow{h\nu} (\pi\text{-cp})Fe(CO)_2HgX$$
$$(X = Cl, Br, I)$$

Insertion of SnX_2 into metal–metal bonds has been observed with Group VI metal complexes (*241*):

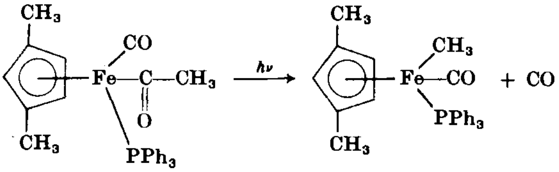
$$[(\pi\text{-cp})M(CO)_3]_2 + SnX_2 \xrightarrow{h\nu} [(\pi\text{-cp})M(CO)_3]_2SnX_2$$
$$(M = Cr, Mo, W; X = F, Cl)$$

Photochemical elimination of N_2 from azide complexes or of triphenylphosphineoxide from nitrosylphosphine complexes leads to the isocyanide complexes **83–85** as a result of CO addition to nitrenes (*379*).



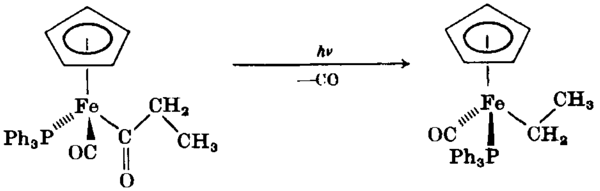
The photoreversal of the addition of olefins to nickel bis (1,2-ethenedithiolates) (*262*), the formation of diphenylacetylene from  $Ph_2C_3{=}Mo(CO)_5$ (*460*), the loss of PR_3 from $[R_3P(C_4H_4)Fe(CO)_2NO]^+PF_6^-$ (*176*), and the production of $[(C_6H_5)_3P]_2N[W(CO)_5Cl]$ from $[(C_6H_5)_3P]_2N[W_2Ni_3(CO)_{16}]$ (*480*) are further examples of *photoelimination* reactions.

The *photochemical decarbonylation* of metal–acyl compounds has generated preparative as well as mechanistic interest, owing to its close relation (principle of microscopic reversibility!) to the important CO insertion reaction (*607*), which has found wide industrial application. The stereochemistry of decarbonylation has been studied using the complex **86**. Separation of the two diastereomeric pairs of enantiomers of **86** led to an enrichment of 95/5 of one over the other (*18*). Photolysis under decarbonylation to **87** produced 88/12 mixtures of the corresponding diastereomeric pairs of **87**.

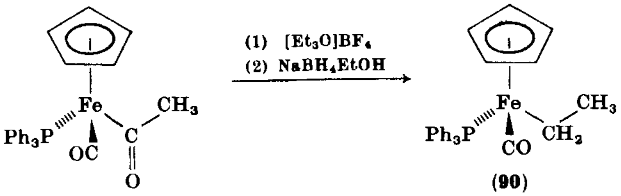


(**86**) (**87**)

From this observation it becomes obvious that the loss of CO occurs with a high degree of stereoselectivity. Earlier work had already shown that in this process a terminal CO and not the acyl–CO group is eliminated, this is followed by migration of the alkyl group to the



(**88**) (**89**)



(**90**)

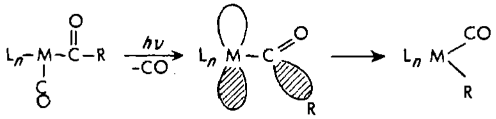
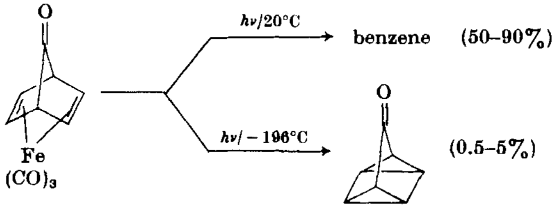


FIG. 13. Photochemical elimination of CO from metal–acyl compounds showing nucleophilic attack on CO—CH_3 σ-bond on metal p orbital.

free coordination site (*4*). This reaction occurs with inversion of configuration at the iron center, as demonstrated by Davison and Martinez, who used **88** of high optical purity (*153*). The configuration of photochemically formed **89** was determined by comparison with **90**.

The fact that photochemical decarbonylation involves inversion at the metal and retention of configuration at the alkyl group (*54*) is consistent with the following explanation: (i) The migrating alkyl group has a high preference for the vacant site produced by elimination of terminal CO; (ii) the cleavage of the acyl bond and the coordination of the alkyl group to the iron have to occur in a concerted fashion; and (iii) the reviewers suggest a nucleophilic attack of the CO–alkyl bond on the vacant site of the iron, as depicted in Fig. 13.

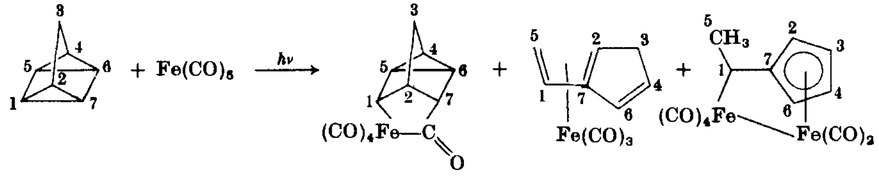
A 1,4-elimination of CO is observed on photolysis of tricarbonyl (7-norbornadienone) iron (**91**) (*360, 361*). Complex **91** is an example of the stabilization by a tricarbonyliron group of an organic moiety, which is highly unstable in the uncomplexed state. On irradiation, carbon monoxide is expelled and appreciable amounts of benzene are formed. At low temperatures quadricyclanone (**92**) was obtained in low yields:



(**91**) (**92**)

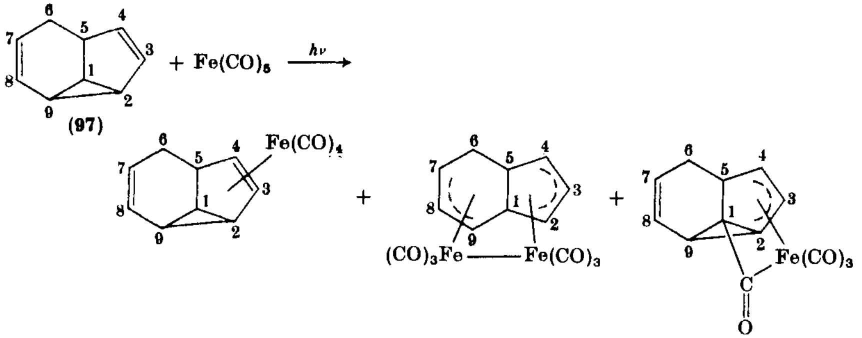
Other decarbonylation reactions of preparative interest include the formation of vinyliron compounds (*406*) and the preparation of h^5-cycloheptatrienyl tricarbonylmanganese (*602*) and of diazaallyl- and 2-azabutadienemanganese complexes (*272, 308*).

Carbonylation reactions are frequently connected with *skeletal rearrangements* and the interested reader is referred to work in this field especially to that by Aumann. Photolysis of $Fe(CO)_5$ in the presence of quadricyclane (**93**) results in skeletal rearrangement of the ligand as well as in CO insertion into a M—C bond (*21*). Although addition of the C-1—C-7 bond in **93** to $Fe(CO)_4$ followed by CO insertion is supposed to give **94**, the formation of **95** and **96** is explained by scission of the C-4—C-5 and C-5—C-6 bonds:



(93) **(94)** **(95)** **(96)**

The same author (*19*) described the light-induced reaction of homosemibullvalene (**97**) with $Fe(CO)_5$:

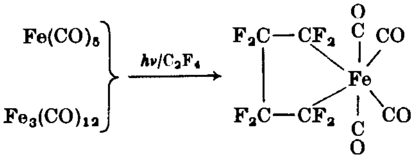


(97)

Further examples for this type of reaction are the photochemical transformations of substituted vinylcyclopropanes, cyclopropylacetylenes, and methylenecyclopropanes in the presence of $Fe(CO)_5$ (*579*, *576*, *603*).

One of the most important functions of transition metals in organometallic catalysis is that of template for the *formation of* C—C *bonds* between coordinated olefins, dienes, etc. As pointed out in Section IV, A, photochemistry is valuable in investigating the mechanism of such reactions at low temperatures.

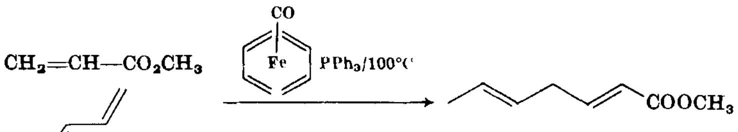
A well-known example of C—C bond formation in a thermal reaction is the production of the ferracyclopentane derivative (**98**). Recently, the photochemical reaction of $Fe(CO)_5$ and $Fe_3(CO)_{12}$ with C_2F_4 has been reported, providing a simple route to **98** (*188*):



(98)

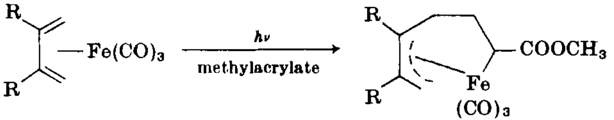
An intermediate $(C_2F_4)Fe(CO)_4$ complex that reacts readily with C_2F_4 to give **98** can be isolated (*189*). Olefins $CF_2{=}CFCl$, $CF_2{=}CFBr$, $CF_3CF{=}CF_2$, and $CF_3CH{=}CF_2$ and cyclic fluoroolefins failed to give ferracyclopentane derivatives.

As already mentioned in Section IV, A, 10, bis(butadiene)mono carbonyliron is a quite efficient catalyst for the mixed oligomerization of dienes and acrylate in the presence of PPh_3 leading to heptadienoic esters (**99**) (*92*):



(99)

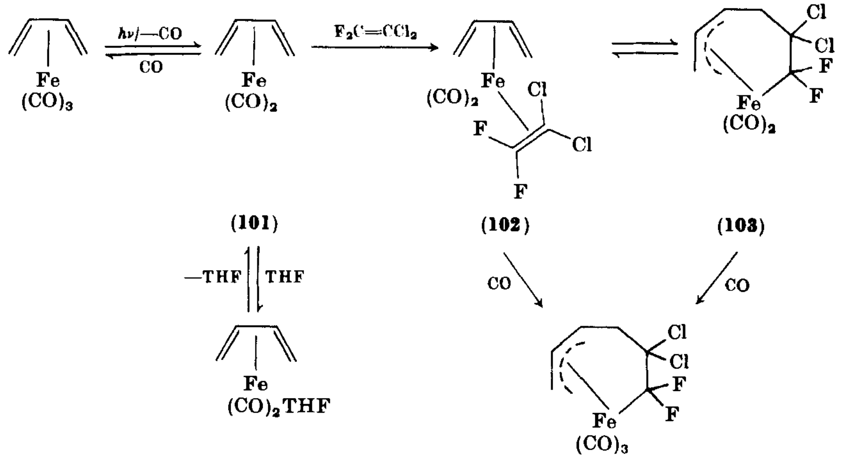
Some insight into the mechanism of this process has been provided by the photochemical reaction of butadienetricarbonyliron and acrylate, leading to **100** (*235*):



(R = H, CH_3)

(100)

A similar reaction has been carried out using 1,1-dichloro-2,2-difluoroethylene (*302*). In the latter case it has been demonstrated by low-temperature irradiation of butadienetricarbonyliron in THF and subsequent addition of $CCl_2{=}CF_2$ in the dark that the carbon–carbon bond formation involves intermediate formation of **101** and **102**. It is



(101) **(102)** **(103)**

still an open question whether C—C bond formation is triggered by the attack of an additional ligand (in this case of CO) following the principles of a S_N2 reaction or whether it occurs via the intermediate **103** (*325*).

Similar cases of C—C bond formation between fluoroolefins (or fluoroketones) with diene-, cyclobutadiene-, and related carbonyliron complexes have been reported by Green *et al.* (*63, 60, 62, 61, 233*; see also Ref. *98*).

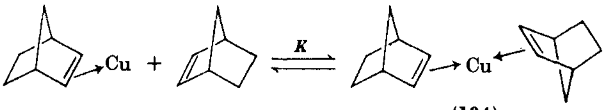
The *photodimerization of norbornene* with Cu halides as catalysts is a well-known reaction (*561*). Recently, the dimerization has been studied in the presence of copper(I)triflate (triflate = trifluoromethanesulfonate) (*483, 484*). This catalyst shows several advantages over Cu halides: The yields of dimers (**106**) were improved significantly and the complex formed from Cu triflate and olefin is thermally stable and soluble in various organic solvents. Under these conditions the mechanism of photodimerization could be investigated in a wide range of olefin concentrations. The proposed mechanism for dimer formation is shown in Eqs. (38)–(40). Contrary to earlier proposals (*561*), the photochemical conversion of the bis(norbornene) complex (**104**) was found to be the key step on the way to **106**.

> The mechanistic details of the collapse of the photoexcited species are not provided by these studies. It is possible that the copper ion in (**104**) facilitates the required absorption of UV light by an otherwise weakly absorbing olefin, and may merely act as a template which promotes a concerted orbital-symmetry allowed photochemical $[2_{\pi s} + 2_{\pi s}]$ cycloaddition.
>
> The metal may alternatively participate in a stepwise process in which a σ-bonded intermediate is formed in a light-induced oxidative metallocycloaddition. In this process, the Cu(I)–bisolefin complex undergoes oxidation to a dialkylcopper intermediate (**105**), which collapses to product by reductive elimination (484).

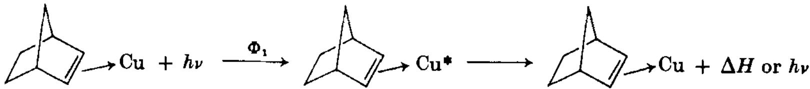
A speculative suggestion for the intermediacy of (**105c**) dates back to 1969 (*332*). Copper triflate serves also as catalyst for the dimerization of cyclopentene, cyclohexene, cycloheptene (*485*), and mixed photodimerization of norbornene and cyclooctene (*484*).

Another important application of Cu_2Cl_2 has been in the improved photochemical synthesis of *trans*-cyclooctene from *cis*-cyclooctene (*164*).

Hardly any ligand in organometallic chemistry has attracted more interest then molecular nitrogen. Although there are numerous complexes containing N_2, successful attempts to reduce N_2 or to incorporate it into organic compounds have been rather scarce. This problem is far from solved; suggestions for a photochemical approach have been put forward (*203*).



(104) (38)



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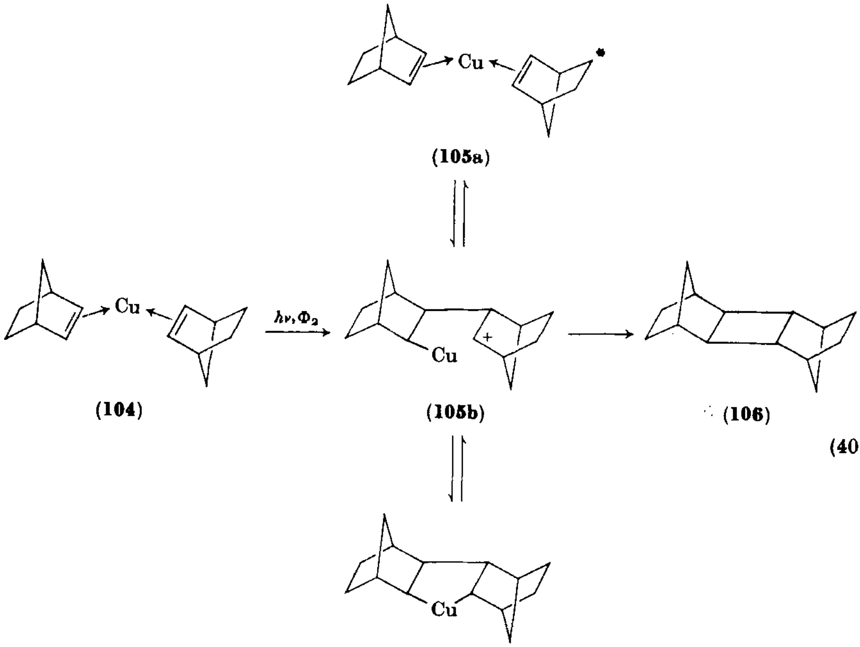


(105a)

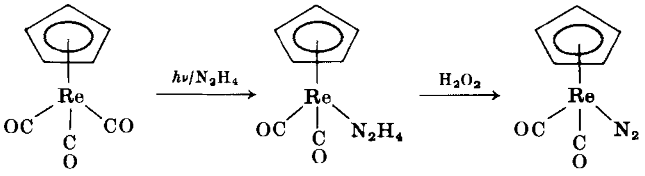
(104) (105b) (106)

(105c)

(40)

Photochemical substitution of CO *by* N_2 (e.g., in arene–tricarbonylchromium) has been accomplished by Sellmann *et al.* (*529*, *530*).

The rhenium N_2 complex (**109**) was not obtained by substitution of CO by N_2 but by introduction of hydrazine in **107** to give **108** and subsequent oxidation of **108** with hydrogen peroxide (*526*):

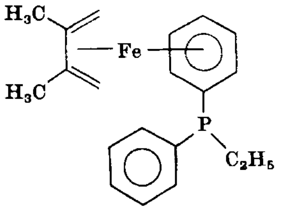


(107) (108) (109)

Photochemically produced hydrazine complexes have also been the starting materials for diimine complexes (*527*, *528*).

The first reports on the photochemical reactions of complexes containing molecular nitrogen as a ligand, have been published. Irradiation of Re(I)–, Os(II)–, Fe(II)–, and Mo(O)–N_2 complexes in the presence of CO leads to N_2 expulsion and formation of metal carbonyl complexes (*146*).

The primary process in the photolysis of $FeH_2N_2(PEtPh_2)_3$ is the cleavage of the metal–dinitrogen bond (*329*). The resulting coordinatively unsaturated intermediate hydrogenates olefins and dienes. Photolysis in the presence of dimethylbutadiene yields, in addition to 2,3-dimethyl-2-butene, the diene–phosphineiron complex (**110**), in which the phosphine is coordinated by the 6π-electron system of a phenyl ring (and not by the phosphorus):



(110)

C. Tabular Survey of Photochemical Substitution Reactions of Metal Carbonyl Compounds with *n* and π Donors and of Photochemical Formation of Metal–Metal Bonds

Reactions of preparative interest have been compiled in Tables IX–XI. Most of the information discussed in the pertinent text has also been included; however, the reader is advised to check also the corresponding sections for additional information.

TABLE IX

Photochemical Substitution Reactions of Metal Carbonyl Compounds with *n* Donors[a,b,c]

I. Coordination via N

Ammonia: $V(CO)_6^-$ (*462*)

Amines: $Mo(CO)_6$ (*565*); $Cr(CO)_5PPh_3$ (*523*); $Mo(CO)_5PPh_3$ (*523*); $W(CO)_5PPh_3$ (*523*)

Hydrazine: (π-cp)$Re(CO)_3$ (*526*)

Nitriles: cycloheptatriene $Cr(CO)_3$ (*12*); $Fe(CO)_5$ (*550*)

Table IX—*Continued*

Hydroxylamine

$\left.\begin{array}{l}\mathrm{Cr(CO)_6}\\ \mathrm{Mo(CO)_6}\\ \mathrm{W(CO)_6}\end{array}\right\}$ only degradation (*89*)

Thiourea derivatives: $[(\pi\text{-cp})Mo(CO)_3]_2$ (*566*); $Mo(CO)_6$ (*566*)

Azomethines: $C_5H_5V(CO)_4$ (*88*); $Cr(CO)_6$ (*89, 589*); $Mo(CO)_6$ (*89, 589*); $W(CO)_6$ (*89*)

Pyridine derivatives: $Cr(CO)_6$ (*157, 459**); cycloheptatriene$Cr(CO)_3$ (*12*); $Mo(CO)_6$ (*157, 565, 459**); (π-cp)$Mo(CO)_3Cl$ (*88*); $Mo(CO)_5PPh_3$ (*523*); $W(CO)_6$ (*157, 459**); (π-cp)$W(CO)_3Cl$ (*88*); $W(CO)_5PPh_3$ (*523*); $C_6F_5Mn(CO)_5$ (*419*); Ru(carbonyl-octaethylporphyrin)pyridinate (*265, 538*)

Imidazole derivatives (L = 1,3-dimethyl-4-imidazoline-2-ylidene): $Cr(CO)_6$ (*210, 40*); $LCr(CO)_5$ (*415*); $Mo(CO)_6$ (*40*); $LMo(CO)_5$ (*415*); $W(CO)_6$ (*210, 40*); $LW(CO)_5$ (*415*)

Pyrazole derivatives: $Cr(CO)_6$ (*210*); $W(CO)_6$ (*210*); $Fe(CO)_5$ (*317*)

Tetrazole derivatives: $Cr(CO)_6$ (*210*); $W(CO)_6$ (*210*)

Thiazoles, isothiazoles, selenazoles: $Cr(CO)_6$ (*210, 601, 40*); $Mo(CO)_6$ (*40, 601*); $W(CO)_6$ (*210, 601, 40*)

Oxazoles: $Cr(CO)_6$ (*210, 601, 40*); $Mo(CO)_6$ (*601, 40*); $W(CO)_6$ (*601, 40*)

SCN^-: $Cr(CO)_6$ (*478*); $W(CO)_6$ (*478*); $Fe(CO)_5$ (*478*)

Other N- ligands

2,3-Diazobicyclo[2.2.1]heptene-2: $Cr(CO)_6$ (*258, 256*); (π-cp)$Mn(CO)_3$ (*256*); trimethylbenzene–$Cr(CO)_3$ (*258, 256*)

$C_5H_5(CO)_2Ru—C_6H_4—N{=}N—C_6H_5$ (intramolecular: (*86*)

$(CO)_3CrC_6H_5—NHR$ (R = H, CH_3):$M(CO)_6$ (M = Cr, Mo, W): (*371*)

Benzocinnoline or phenanthridine

$\left.\begin{array}{l}\mathrm{Cr(CO)_6}\\ \mathrm{Mo(CO)_6}\\ \mathrm{W(CO)_6}\end{array}\right\}$ (*323*)

$Ph_2C{=}NLi$

$\left.\begin{array}{l}(\pi\text{-cp})\mathrm{Mo(CO)_3Cl}\\ (\pi\text{-cp})\mathrm{W(CO)_3Cl}\end{array}\right\}$ (*295*)

(continued)

Table IX—*Continued*

II. Coordination via P

Aromatic Phosphines (monodentate)

$$\left.\begin{array}{l}V(CO)_6^-\\ Nb(CO)_6^-\\ Ta(CO)_6^-\end{array}\right\}(\mathit{151})$$

Norbornadiene–$Cr(CO)_4$ (*438*); cycloheptatriene–$Cr(CO)_3$ (*12*); $(C_6H_5CO_2CH_3)Cr(CO)_2L$ (L = CO, CS) (*279, 277, 278*); $[C_6H_4(CO_2CH_3)_2]Cr(CO)_3$ (*551*); $(C_6H_5CO_2$–menthyl)$Cr(CO)_3$ (*278*); $(C_6H_5CO_2H)Cr(CO)_3$ (*278*); (*t*-Bu—$C_6H_4CO_2CH_3)Cr(CO)_3$ (*278*); (*t*-Bu—$C_6H_4CO_2$–menthyl)$Cr(CO)_2$ (*278*); $(CH_3C_6H_5)Cr(CO)_3$ (*370*); $(Et_2N$—$C_6H_5)Cr(CO)_3$ (*370*); $(CO)_5Cr[CR'R'']$ (R′ = OCH_3, OC_2H_5; R″ = CH_3, C_2H_5) (*195*); $Cr(CO)_5PPh_3$ (*523*); $Mo(CO)_6$ (*38**); $CF_3Mo(CO)_3$(π-cp) (*310*); $Mo(CO)_5PPh_3$ (*523*); $Mo(CO)_5NHC_5H_{10}$ (*523*); $W(CO)_6$ (*83*); $W(CO)_5PPh_3$ (*523*); $W(CO)_5NC_5H_5$ (*523*); $[Ph_3PNPPh_3][CF_3CO_2W(CO)_5]$ (*493*); $(CO)_5W[CR'R'']$ (*195*); (π-$RC_5H_4)Mn(CO)_3$ (R = C_2H_5, Ph—CH_2, Cl, Br, I, $COOCH_3$, COOH, $COCH_3$) (*356, 304*); indenyl– and fluorenyl–$Mn(CO)_3$ (*305*); pyrrolyl–$Mn(CO)_3$ (*306*); (π-cp)$Mn(CO)_2R$ (R = CO, CS) (*87**, *129**); $Mn_2(CO)_{10}$ (*383*, *357**); Mn $(CO)_5Br$ (*385**); $Re_2(CO)_{10}$ (*384**, *535**); $Fe(CO)_5$ (*497, 550, 121*); R—Fe(π-cp)$(CO)_2$ (R = CF_3, CF_3CO, C_2F_5, $(CF_3)_2CF$) (*310*); $[Fe(CO)_3SC_6H_5]_2$ (*156*); (π-cp)$Fe(CO)_2CH_2OCH_3$ (*152*); (π-cp)$Fe(CO)_2SnR_3$ (*139, 142*); (π-cp)$Fe(CO)_2SiR_3$ (*123*); (π-cp)$Fe(CO)_2$—σ—C_5H_4—Fe(π-cp) (*403*); (π-cp)$Fe(CO)_2(C_6H_4F)$ (*397, 408*); $Ru_3(CO)_{12}$ (*286*)

Aliphatic phosphines (monodentate): $V(CO)_6^-$ (*151*); (π-cp)$V(CO)_4$ (*199*); $Cr(CO)_6$ (*377**, *376**, *551, 511, 515, 517*); $[C_6H_4(CO_2CH_3)_2]Cr(CO)_3$ (*551*); mesitylene–$Cr(CO)_3$ (*551*); hexamethylbenzene–$Cr(CO)_3$ (*551*); benzene $Cr(CO)_3$ (*551*); $Mo(CO)_6$ (*377**, *376**, *551, 511, 515, 517*); $W(CO)_6$ (*377**, *376**, *551, 511, 515, 517*); (π-$R_5C_5)Mn(CO)_3$ (R = CH_3, H) (*516, 517*); $Fe(CO)_5$ (*497*, *550**, *517, 518, 121*); [2-5-η-(5-phenylpenta-2,4-dienal)]–$Fe(CO)_3$ (*75*)

Aromatic phosphines (bidentate)

$$\left.\begin{array}{l}V(CO)_6^-\\ Nb(CO)_6^-\\ Ta(CO)_6^-\end{array}\right\}(\mathit{151})$$

$Cr(CO)_6$ (*487*); $Mo(CO)_6$ (*487*); $CF_3Mo(CO)_3$(π-cp) (*310*); R—Fe(π-cp)$(CO)_2$ [R = C_2F_5, $(CF_3)_2CF$] (*310*); (π-cp)$_2Fe_2(CO)_4$ (*108, 109*); [(π-cp)$Fe(CO)_2(OCMe_2)]^+$ (*82*); $W(CO)_6$ (*487*); $Mn_2(CO)_{10}$ (*464, 135*); $Mn(CO)_5Br$ (*464*); (π-cp)$Mn(CO)_3$ (*228*); $Re_2(CO)_{10}$ (*135*); $Fe(CO)_5$ (*138, 139, 121*); $Fe_3(CO)_{12}$ (*138*); $[Fe(CO)_3\text{-}SC_6H_5]_2$ (*156*); (π-cp)$Fe(CO)_2SnR_3$ (*139*); $Ru_3(CO)_{12}$ (*137*)

Aliphatic phosphines (bidentate): $Cr(CO)_6$ (*73, 46*); $Mo(CO)_6$ (*73*); $W(CO)_6$ (*73*); $Fe(CO)_5$ (*7*)

Polydentate phosphines: $Cr(CO)_6$ (*130*); (π-cp)$Mo(CO)_3Cl$ (*309*); $W(CO)_6$ (*130*); $Mn_2(CO)_{10}$ (*182*); (π-cp)$Mn(CO)_3$ (*311, 313*); (π-cp)$Fe(CO)_2Br$ (*309*); $Co_2(CO)_8$ (*431**)

Table IX—*Continued*

Phosphorus ylides: $W(CO)_6$ (*292, 539*); $Mo(CO)_6$ (*539*); $Cr(CO)_6$ (*539*)

Phosphites: $Cr(CO)_6$ (*271, 377, 376**); $(C_6H_6)Cr(CO)_3$ (*394*); mesitylene–$Cr(CO)_3$ (*551*); hexamethylbenzene–$Cr(CO)_3$ (*551*); $(C_6H_5—CO_2R)Cr(CO)_2L$ ($R = H, CH_3$; $L = CO, CS$) (*278, 276, 279*); $(CH_3—C_6H_4CO_2R)Cr(CO)_2L$ ($R = CH_3, H$; $L = CO, CS$) (*278, 276, 279*); cycloheptatriene–$Cr(CO)_3$ (*12*); $Mo(CO)_6$ (*271, 377*); $W(CO)_6$ (*271, 377, 376*, 83, 551*); $(\pi\text{-cp})Mn(CO)_2R$ ($R = CO, CS$) (*129**); $(\pi\text{-}C_5H_3R^1R^2)Mn(CO)_3$ ($R^1 = CH_3, R^2 = CO_2CH_3$) (*366**); $CH_3CO—Mn(CO)_3\text{-}[P(OCH_3)_3]_2$ (*562*); $Fe(CO)_5$ (*497, 550*, 121*); $[Fe(CO)_3SC_6H_5]_2$ (*156**); $(C_4H_4)Fe(CO)_3$ (*201**)

PH_3: $Cr(CO)_6$ (*198**); $Mn_2(CO)_{10}$ (*197*); $ONCo(CO)_3$ (*482*)

PF_3 (and other PX_3; X = halogen): $V(CO)_6^-$ (*346**); $Cr(CO)_6$ (*390*, 551*); $(PF_3)_3Cr(CO)_3$ (*365**); $(PF_3)_3Mo(CO)_3$ (*365**); $(PF_3)_3W(CO)_3$ (*365**); $(\pi\text{-cp})Mn(CO)_3$ (*390*, 351*, 497**); $Fe(CO)_5$ (*571*, 497**); butadiene–$Fe(CO)_3$ (*596**); cyclohexadiene–$Fe(CO)_3$ (*595**); trimethylenemethane–$Fe(CO)_3$ (*116**); $RCo(CO)_4$ ($R = CF_3, C_2F_5, C_3F_7$) (*570**)

$PX_{3-n}R_n$ (X = halogen): $Cr(CO)_6$ (*180, 540*, 377**); $Mo(CO)_6$ (*180, 540*, 377**); $W(CO)_6$ (*180, 540*, 377*, 213*); $(\pi\text{-cp})Mn(CO)_3$ (*314**)

$P(NR_3)_3$: $Cr(CO)_6$ (*312**); $W(CO)_6$ (*312**)

$PR_{3-n}L_n$ (L = organometallic derivatives; n = 1–3): $Cr(CO)_6$ (*511*, 515, 517*); $Mo(CO)_6$ (*511*, 515, 517*); $W(CO)_6$ (*511*, 515, 517*); $(\pi\text{-}C_5H_4R)Mn(CO)_3$ ($R = H, CH_3$) (*516, 517*); $Fe(CO)_5$ (*518, 517*)

Triferrocenylphosphine: π-cp $Mn(CO)_3$ (*401*); $C_6H_6Cr(CO)_3$ (*401*)

III. Coordination via As, Sb, Bi

Arsines, stibines, bismuthines (monodentate): $V(CO)_6^-$ (*151*); $Cr(CO)_6$ (*510, 192, 551, 508, 514, 84*); $[C_6H_4(CO_2CH_3)_2]Cr(CO)_3$ (*551*); $Mo(CO)_6$ (*38*, 508, 514, 192, 84, 510*); $W(CO)_6$ (*510, 84, 192, 551, 508, 514, 83*); norbornadiene–$W(CO)_4$ (*312*); fluorenyl- and indenyl-$Mn(CO)_3$ (*305*); pyrrolyl-$Mn(CO)_3$ (*306*); $Mn_2(CO)_{10}$ (*357**); $(\pi\text{-cp})Mn(CO)_2CS$ (*129*); $Re_2(CO)_{10}$ (*535**); $Fe(CO)_5$ (*550, 192, 139, 121*); $(\pi\text{-cp})Fe(CO)_2SnR_3$ (*139, 142*); $Fe_3(CO)_{12}$ (*112*)

Arsines (bidentate): $Cr(CO)_6$ (*487**); $Mo(CO)_6$ (*487**); $W(CO)_6$ (*487**); $(\pi\text{-}C_5H_4R)\text{-}Mn(CO)_3$ ($R = H, CH_3$) (*486*); $Mn_2(CO)_{10}$ (*135*); $Re_2(CO)_{10}$ (*135*)

$As(NR_3)_3$: $Cr(CO)_6$ (*312*); $W(CO)_6$ (*312*); norbornadiene–$W(CO)_4$ (*312*); $Fe(CO)_5$ (*139, 141*); $Fe_3(CO)_{12}$ (*112, 140*); $Ru_3(CO)_{12}$ (*137*)

Arsines and stibines with organometallic ligands: $Cr(CO)_6$ (*509, 510, 514*); $Mo(CO)_6$ (*509, 510, 514*); $W(CO)_6$ (*509, 510, 514*); $(\pi\text{-cp})Mn(CO)_3$ (*514*); $Fe(CO)_5$ (*514*)

(*continued*)

Table IX—*Continued*

$AsR_{3-n}X_n$ (X = halogen): $Cr(CO)_6$ (*180, 551*); $Mo(CO)_6$ (*180*); $W(CO)_6$ (*180*)

Mixed phosphine–arsine ligands (coordination via P and As): $Fe(CO)_5$ (*112*); $Fe_2(CO)_9$ (*112*)

IV. Coordination via O

Alcohols; ketones: $W(CO)_6$ (*83, 620*)

Ethers: $V(CO)_6^-$ (*71*); $W(CO)_6$ (*83*)

Other oxygen compounds: ethyl acetate + $Mo(CO)_6$ (*33*); benzisoxazole + $W(CO)_6$ (*601*)

V. Coordination via S, Se, Te

Thioethers, Thiophenols: $Cr(CO)_6$ (*519*); $Mo(CO)_6$ (*519*); $W(CO)_6$ (*519, 83*)

$R_3P{=}S$ and $R_3As{=}S$: $Cr(CO)_6$ (*2, 3, 369*); $Mo(CO)_6$ (*369*); $W(CO)_6$ (*2, 3*)

R—S—R′ (R = metalorganic ligand; R′ = R, alkyl, aryl): (π-cp)$V(CO)_4$ (*179*); $Cr(CO)_6$ (*181, 519*); $Mo(CO)_6$ (*179, 519, 324*); $W(CO)_6$ (*179, 519*)

Other sulfur ligands: thiazolidine-2-thione + $M(CO)_6$ (M = Cr, Mo, W) (*162*); 2-methyl-4,5-benzothiazoline + $Cr(CO)_6$ (*601*); thioformaldehyde trimer: $Cr(CO)_6$ (*495*); $Mo(CO)_6$ (*495*); thiomorpholin-3-thione: $Cr(CO)_6$ (*163*); $Mo(CO)_6$ (*163*); $W(CO)_6$ (*163*); thiomorpholin-3-one: $Cr(CO)_6$ (*432**); $Mo(CO)_6$ (*432**); $W(CO)_6$ (*432**); thiocyclobutene: $Fe(CO)_5$ (*555, 556*); $[M(CO)_5NCS]^-$ (M = Cr,W): $Mo(CO)_6$ (*43*); $W(CO)_6$ (*43*); (π-cp)$Ru(CO)_2SR$: (π-cp)$Ru(CO)_2SR$ (*319*)

Selenides and tellurides

$$\left.\begin{array}{l}Cr(CO)_6\\ Mo(CO)_6\\ W(CO)_6\end{array}\right\}(512,\ 513,\ 520)$$

VI. Coordination via C

^{13}CO and $C^{18}O$: (π-cp)$V(CO)_4$ (*99*); $Mo(CO)_5NHC_5H_{10}$ (*145*); $Mo(CO)_5PPh_3$ (*523*); $W(CO)_5NHC_5H_{10}$ (*523*); $W(CO)_5PPh_3$ (*523*); $Mn_2(CO)_{10}$ (*296, 65*); $Mn(CO)_5Br$ (*47*); (π-cp)$Mn(CO)_3$ (*99*); $Fe(CO)_5$ (*296*, 411*, 66*); $Fe_3(CO)_{12}$ (*296**); butadiene–$Fe(CO)_3$ (*596**); $Co_2(CO)_8$ (*296**); $Co_4(CO)_{12}$ (*296**); (π-cp)$Co(CO)_2$ (*99**)

CN^-: $V(CO)_6^-$ (*462*); $Cr(CO)_6$ (*478*); $W(CO)_6$ (*478*); (π-$(CH_3)_5C_5$)$Mn(CO)_3$ (*166*); $Fe(CO)_5$ (*478*)

Carbenes: $Fe(CO)_5$ (*193, 194*)

Table IX—*Continued*

VII. Coordination of Special Ligands

Ligand	Starting material	Ref.
NO	(π-cp)$V(CO)_4$	*259*
	$Cr(CO)_6$	*259, 553*
	$Fe(CO)_5$	*259*
	$Mn_2(CO)_{10}$	*259, 260*
H_2	$Fe(CO)_3(PPh_3)_2$	*572*
	$Fe_3(CO)_{10}NSi(CH_3)_3$	*330*
	$Ru(CO)_3(PPh_3)_2$	*572*
	$Os(CO)_3(PPh_3)_2$	*572*
SiI_4	$Fe(CO)_5$	*494*
Carboranes,	$Cr(CO)_6$	*598, 42, 532*
boranes,	$Mo(CO)_6$	*598, 42, 532, 175*
phosphacarboranes,	$W(CO)_6$	*598, 42, 532, 175*
azacarboranes	$Re(CO)_5Br$	*209*
	$Fe(CO)_5$	*154, 207, 41*
	(π-cp)$Fe(CO)_2I$	*209*
Thio- and seleno-ketocarbenes	$Fe(CO)_5$	*501*

[a] In Parts I–VI of this table, references are given in parentheses with compounds.

[b] (π-cp) = [1-5-η-cyclopentadienyl].

[c] * indicates substitution by more than one ligand.

TABLE X

PHOTOCHEMICAL SUBSTITUTION REACTIONS OF METAL CARBONYL COMPOUNDS WITH π DONORS[a,b]

Ligand	$M(CO)_n$	Ref.
I. Monoolefins: $M(CO)_{n-1}L$, $M(CO)_{n-2}L_2$ (L = olefin)		
Ethylene	(π-cp)$_2$MoCO	*558*
	$Ph_3SnFe(CO)_2$(π-cp)	*342*
	$Ru_3(CO)_{12}$	*289*
Tetrafluoroethylene (and other	$Fe(CO)_5$, $Fe_3(CO)_{12}$	*188, 190*
fluorinated olefins)	$Os(CO)_3[P(OCH_3)_3]_2$	*122*
Tetramethoxyethylene	(π-cp)$Mn(CO)_3$	*254*
Cyclopentene	$(H_3C)_6C_6Cr(CO)_3$	*13*
Cyclooctene	(π-$C_6H_5CO_2CH_3$)$Cr(CO)_3$	*276, 278*
	Cycloheptatriene $Cr(CO)_3$	*12*
	(π-cp)$Mn(CO)_2CS$	*186, 185*
	(π-cp)$MnCO(CS)_2$	*186, 185*
2-Vinylaziridine	$Fe(CO)_5$	*21*

(*continued*)

Table X—*Continued*

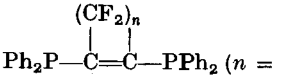
Ligand	M(CO)$_n$	Ref.
2-Vinyloxirane	Fe(CO)$_5$	*21*
Vinylcyclopropane	Fe(CO)$_5$	*20*
Homosemibullvalene	Fe(CO)$_5$	*19*
Allylchloride	Na[V(CO)$_6$]	*496*
Allyltrifluoroacetate	Mo(CO)$_6$	*155*
	W(CO)$_6$	*155*
Maleic acid	[(CH$_3$)$_6$C$_6$]Cr(CO)$_3$	*13*
Fumaric acid	[(CH$_3$)$_6$C$_6$]Cr(CO)$_3$	*13*
Dimethylmaleate	(C$_4$H$_4$)Fe(CO)$_3$	*461*
Dimethylfumarate	(C$_4$H$_4$)Fe(CO)$_3$	*594*
Fumaric acid dinitrile	Cr(CO)$_6$	*192*
	Mo(CO)$_6$	*192*
	W(CO)$_6$	*192*
Maleimide	(C$_6$H$_6$)Cr(CO)$_3$	*394*
Maleic anhydride	[(CH$_3$)$_6$C$_6$]Cr(CO)$_3$	*13*
	(π-cp)Mn(CO)$_3$	*257*
	Substituted ArCr(CO)$_3$	*255, 257*
Acrylonitrile	(π-cp)$_2$MoCO	*558*
Acrylic acid	Fe(CO)$_5$	*121*
Methylacrylate	Fe(CO)$_5$	*237*
Endic anhydride	[(CH$_3$)$_6$C$_6$]Cr(CO)$_3$	*13*
Citraconic anhydride	[(CH$_3$)$_6$C$_6$]Cr(CO)$_3$	*13*
trans-Benzalacetophenone	Fe(CO)$_5$	*333*
(3-Butenyl)diphenylphosphine	Mo(CO)$_6$	*211*
	Mo(CO)$_4$norbornadiene	*211*
	Mo(CO)$_4$Cl$_2$	*211*
	Mo(CO)$_3$cycloheptatriene	*211*
 $\overset{(CF_2)_n}{Ph_2P{-}C{=}C{-}PPh_2}$ (n = 2–4)	Ru$_3$(CO)$_{12}$	*137*
Thiacyclobutene	Fe(CO)$_5$	*555, 556*
1-Methyl-2R-1,2-dihydropyridazine-3,6-dione	Fe(CO)$_5$	*407*
(π-cp)Fe(CO)$_2$—CH$_2$CR$_2$—CH=CH$_2$	Intramolecular	*234*
II. Dienes: LM(CO)$_{n-2}$, etc. (L = diene)		
1,3-Butadiene	Fe(CO)$_5^*$	*326, 327, 340*
	R$_3$MFe(CO)$_2$(π-cp) (M = Sn, Pb, Ge; R = CH$_3$, Ph)	*399, 398*
	(π-cp)Mn(CO)$_3$	*196*
Isoprene	Fe(CO)$_5^*$	*327, 326*
1,3-Pentadiene	[C$_7$H$_9$Fe(CO)$_3$]BF$_4$	*16*
trans,trans-2,4-Hexadiene	Cr(CO)$_6$	*328*
	Fe(CO)$_5^*$	*92*
Dimethylbutadiene	Fe(CO)$_5^*$	*326*

Table X—*Continued*

Ligand	$M(CO)_n$	Ref.
	$FeH_2N_2(PEt\ Ph_2)_3$	*329*
Cyclopentadiene	(π-cp)$Mn(CO)_3$	*39*
1,3-Cyclohexadiene	$Fe(CO)_5^*$	*327, 326*
	$[C_6H_7Fe(CO)_3]BF_4$	*16*
	$[C_7H_9Fe(CO)_3]BF_4$	*16, 288*
	$[C_8H_{11}Fe(CO)_3]BF_4$	*10*
	(π-cp)$Mn(CO)_3$	*196*
1,3-Cyclohexadiene	$[CH_3OC_6H_6Fe(CO)_3]BF_4$	*16*
1,3-Cycloheptadiene	$[C_6H_7Fe(CO)_3]BF_4$	*16*
	$[C_7H_9Fe(CO)_3]BF_4$	*16*
1,5-Cyclooctadiene	$Cr(CO)_6$	*315*
	$Fe(CO)_5$	*336, 161*
	$Os_3(CO)_{12}$	*127*
1,3-Cyclooctadiene	$Fe(CO)_5$	*336, 161*
	$Cr(CO)_6$	*315*
	$Ru_3(CO)_{12}$	*127*
	$Os_3(CO)_{12}$	*127*
Bicyclo[5.1.0]-2,4-octadiene	$Fe(CO)_5$	*77*
syn-7-Acetoxybenzonorbornadiene	$[(H_3C)_5C_5]Mn(CO)_3$	*600*
Sorbic acid (methyl ester)	$Fe(CO)_5^*$	*326, 92*
Muconic esters	$Fe(CO)_5^*$	*92*
Dihydroacetophenone	$Fe(CO)_5$	*274*
Dihydrobenzaldehyde	$Fe(CO)_5$	*274*
α-Pyrone	(π-cp)$Co(CO)_2$	*473*
Thiophene-1,1-dioxide	$Fe(CO)_5$	*114*
Alkoxydivinylborane–$Fe(CO)_4$	Intramolecular	*261*

III. Cyclic trienes and tetraenes

Ligand	Starting material	Ref.
Cycloheptatriene	$C_4H_4Fe(CO)_3$	*594*
	(π-C_5H_4R)—$Mn(CO)_3$ (R = H, CH_3)	*423*
1,3,5-Cyclooctatriene	(π-cp)$Mn(CO)_3$	*423*
cis-Bicyclo[6.1.0]-nonatriene	$Fe(CO)_5$	*458, 498*
Bicyclo[6.2.0]-1,3,5,-decatriene	$Fe(CO)_5$	*498*
Cyclooctatetraene	(π-cp)$Mn(CO)_3$	*423*
	$Os_3(CO)_{12}$	*85*
N-Carbethoxyazepine	$C_4H_4Fe(CO)_3$	*594*

IV. Acetylenes

Cyclooctyne	$Mo(CO)_6$	*343*
	$Fe(CO)_5$	*344*

(*continued*)

Table X—*Continued*

Ligand	Starting material	Ref.
R—C≡C—R (R = H, CH_3, Ph)	$(\pi\text{-cp})_2MoCO$	*558*
(R = Ph)	$(\pi\text{-cp})W(CO)_3Ph$	*56*
	$[(\pi\text{-cp})Fe(CO)_2]_2$	*400*
	Pyrrolyl–$Mn(CO)_3$	*306*
Dimethylacetylenedicarboxylate	$C_4H_4Fe(CO)_3$	*594*
V. Aromatic compounds		
Substituted styrenes	$Fe(CO)_5$	*581, 577, 578, 580*
Benzocyclobutadiene–$Fe(CO)_3$	$Fe(CO)_5$	*575*
Hexaalkyborazole	$Cr(CO)_6$	*160*
Benzene	$(\pi\text{-cp})Mn(CO)_3$	*423, 196*
VI. Heterodienes and aromatic heterocycles		
Pinocarvone	$Fe(CO)_5$	*333*
Pulegone	$Fe(CO)_5$	*333*
Isobutylidene–Meldrums acid–$Fe(CO)_4$	Intramolecular	*338*
β-Substituted vinylketones	$Fe(CO)_5$	*481, 474, 405*
R—CH=CHCOFe$(CO)_2(\pi\text{-cp})$	Intramolecular	*406*
Ph_3P=CH—CR=CH_2	$Mo(CO)_6$	*539*
2,4,6-Triphenylphosphorine	$Cr(CO)_6$ $Mo(CO)_6$ $W(CO)_6$	*158, 159*

[a] $(\pi\text{-cp})$ = [1-5-η-cyclopentadienyl].

[b] * indicates substitution by more than one ligand.

TABLE XI

PHOTOCHEMICAL FORMATION OF METAL–METAL BONDS[a]

Starting material	Product	Ref.
I. M—M bonds		
$Cr(CO)_5PPh_2H$	$Cr_2(CO)_8(PPh_2)_2$	*564*
$(CH_3)_5C_5Mo(CO)_3CH_3$	$[(CH_3)_5C_5Mo(CO)_2]_2$	*307*
$Mo(CO)_5PPh_2H$	$Mo_2(CO)_8(PPh_2)_2$	*564*
$(\pi\text{-cp})Mo(CO)_3Cl$	$[(\pi\text{-cp})Mo(CO)_2Cl]_2$	*5*
$(\pi\text{-cp})Mo(CO)_2PR_3Cl$	$[(\pi\text{-cp})Mo(CO)_2Cl]_2$	*6*
$(CH_3)_2(CH_2{=}CH)GeMo(\pi\text{-cp})(CO)_2$	$[(\pi\text{-cp})Mo(CO)_2]_2$	*286*
$W(CO)_5PPh_2H$	$W_2(CO)_8(PPh_2)_2$	*564*
$(\pi\text{-cp})W(CO)_3Cl$	$[(\pi\text{-cp})W(CO)_2Cl]_2$	*5*
$(\pi\text{-cp})W(CO)_2PR_3Cl$	$[(\pi\text{-cp})W(CO)_2Cl]_2$	*6*
$(CH_3)_2ClGeMn(CO)_5$	$[(CH_3)_2GeMn(CO)_4]_2$	*144, 286*
$HGePh_2Mn(CO)_5$	$[Ph_2GeMn(CO)_4]_2$	*120*

Table XI—*Continued*

Starting material	Product	Ref.
$(\pi\text{-cp})Re(CO)_3$	$(\pi\text{-cp})_2Re_2(CO)_5$	*206*
$[Fe(CO)_4PPh_2]Li$	$Fe_2(CO)_6(PPh_2)_2$	*564*
$[(\pi\text{-cp})Fe(CO)_2Cl]$	$[(\pi\text{-cp})Fe(CO)_2]_2$	*5*
$[(\pi\text{-cp})FeCOP(OPh)_3]Br$	$[(\pi\text{-cp})Fe(CO)_2]_2$	*6*
$(CH_3)_2(CH_2{=}CH)GeFe(\pi\text{-cp})(CO)_2$	$[(\pi\text{-cp})FeCO]_2COGe(CH_3)_2$	*287, 285*
$(CH_3)_2ClGeFe(\pi\text{-cp})(CO)_2$	$[(CH_3)_2GeFe(\pi\text{-cp})CO]_2CO$	*144*
$Fe(CO)_4PR_2H$	$Fe_2(CO)_6(PR_2)_2$	*563*
$(Cot)Fe(CO)_3$	$(Cot)Fe_2(CO)_5$	*521*
$C_4H_4Fe(CO)_3$	$(C_4H_4)_2Fe_2(CO)_3$	*201*
$(Ph_4C_4)Fe(CO)_3$	$(Ph_4C_4)_2Fe_2(CO)_3$	*391*
$[Ph_2(t\text{-but})_2C_4]Fe(CO)_3$	$[Ph_2(t\text{-but})_2C_4]_2Fe_2(CO)_3$	*391*
$Fe(CO)_5$ (prot. solvent)	$[HFe_3(CO)_{11}]^-$	*290*
$(\pi\text{-cp})Fe(CO)_2P(CF_3)_2$	$[(\pi\text{-cp})Fe(CO)P(CF_3)_2]_2$	*168, 167*
$(\pi\text{-cp})Fe(CO)_2P(O)(CF_3)_2$	$(\pi\text{-cp})_2Fe_3(CO)_2[OP(CF_3)_2]_4$	*168, 167*
$(CO)_4Fe{-}P(CH_3)_2{-}Fe(CO)_2(\pi\text{-cp})$	$(\pi\text{-cp})Fe_2(CO)_5P(CH_3)_2$	*176a*
$(CO)_4Fe{-}PPh_2{-}Fe(CO)_2(\pi\text{-cp})$	$(\pi\text{-cp})Fe_2(CO)_5PPh_2$	*244, 242, 245*
$(CH_3)_2ClCo(CO)_4$	$[(CH_3)_2GeCo(CO)_3]_2$	*144*
$(\pi\text{-cp})Co(CO)_2$	$(\pi\text{-cp})_2Co_2(CO)_3$	*587*
$[(CO)_4Co]_2GePh_2$	$[(CO)_7Co_2]GePh_2$	*118*
$Ru(CO)_5$	$Ru_3(CO)_{12}$	*101*
$(\pi\text{-cp})Ru(CO)_2SR$	$[(\pi\text{-cp})Ru(CO)SR]_2$	*319*
$[FeRu(\pi\text{-cp})_2(CO)_4PPh_2]B(C_6H_5)_4$	$[Ru(\pi\text{-cp})(CO)_2]_2$	*242*
$Os(CO)_5$	$Os_3(CO)_{12}$	*101*
	$Os_2(CO)_9$	*389*

II. Formation of M—M′ bonds

M	M′	Ref.
Ge	$Cr(CO)_6$	*605*
	$Mo(CO)_6$	*605*
	$W(CO)_6$	*605*
	$(\pi\text{-cp})Mn(CO)_3$	*477*
	$Ru_3(CO)_{12}$	*320*
	$Os_3(CO)_{12}$	*320*
Sn	$(\pi\text{-cp})Mn(CO)_3$	*477*
Si	$Ru_3(CO)_{12}$	*76*
	$Os_3(CO)_{12}$	*76*
Mo	$(CO)_4Fe{-}As(CH_3)_2{-}ML_n$	*177*
W	—	*177*
Mn	—	*177*
Co	—	*177*

[a] $(\pi\text{-cp})$ = [1-5-η-cyclopentadienyl].

[b] Cot = Cyclooctatetraene.

V. Biological Applications of Organometallic Photochemistry

The light reaction of photosynthesis in green plants and bacteria appears to be the most sophisticated and efficient application of some of the basic photochemical principles discussed in the previous sections. The turnover of material in photosynthesis has been estimated to exceed the sum of all industrial processes by $\sim 10^2$ (*490*). All our fossil fuels result from that source. An organometallic photochemist, interested in the conversion of "dependable" sun energy (*250*, *455*) and its storage in the form of chemical compounds, should, therefore, try to learn how nature makes photochemical use of metal-containing systems.

Here we focus attention on those parts of the photosynthetic light reaction involving transition metals and on a number of applications of photochemistry to other branches of biochemistry. The photochemical study of hemoglobin and vitamin B_{12} and its model compounds is important in understanding the function of these systems, although they do not act photochemically in nature. By discussing these examples, we hope to demonstrate the importance of the mechanistic principles outlined earlier, and to show, from the viewpoint of an organometallic chemist, the role they play in biological systems.

A. Deactivation of Excited States

In Section III we briefly discussed the effect of transition metals on the lifetime and intersystem crossing rates of systems. The significance of deactivation processes (leading to stability toward light) induced by incorporation of transition metals into bio-organic molecules is demonstrated by the following two examples.

The importance of the fact that chlorophyll, but not hemoglobin, undergoes certain photochemical reactions becomes obvious when the resistance of our blood toward light is considered. Incorporation of iron instead of magnesium into the porphyrin framework must result in significantly accelerated energy dissipation of electronically excited states.

This can be also deduced from a comparison of excited-state emission and lifetime data for some porphyrin complexes (*40a*). Magnesium etioprophyrin shows strong fluorescence as well as phosphorescence, the triplet lifetime being 160 msec. By contrast, iron(II) mesoporphyrin dimethyl ester does not fluoresce; it shows very weak phosphorescence and the triplet lifetime is < 0.5 msec. The metal-free mesoporphyrin dimethyl ester shows weak phosphorescence and its triplet state lifetime is 14 msec (*40a*). An explanation of these phenomena can be sought in low-lying *d-d* states of the iron system that accept the energy of porphyrin-localized excited states and dissipate it efficiently. (See Section IV, D for further discussion of such internal conversion phenomena.)

The relevance of iron for the behavior of our blood toward light becomes clear if it is no longer incorporated into the porphyrin in sufficient amounts. The photoexcited porphyrin is then a very efficient sensitizer for the production by energy transfer of oxygen in its reactive singlet state. Singlet oxygen attacks cholesterol in membranes of red blood cells and the resulting hydroperoxide (*491*) causes their hemolysis. The result is a disease known as erythropoietic protoporphyria (*170*). The most efficient cure is a large dose of β-carotene, which functions as a quencher.

Another case may illustrate how efficiently nature makes use of radiationless deactivation. The very light-resistant violet color of the primaries of the African Turaco bird is due to the incorporation of copper into a porphyrin system, which probably results in very efficient radiationless deactivation (*472*). Copper is widely used in dye chemistry to increase the light resistance of dyes (*632, 191*).

B. PHOTOSYNTHESIS

Energy transfer and electron transfer, which we have discussed in Section III, is of the utmost importance in photosynthesis (*455*). The photosynthetic apparatus of green plants consists of two different photosystems (PS I and PS II).† The PS are basically made up of several hundred chlorophyll (Chl) molecules, which absorb the light (antenna chlorophyll) and guide the electronic excitation to one reactive center (RC). Efficient energy transfer (by excitation interaction) in the antenna chlorophyll is thought to be arranged by lining up the chlorophyll molecules via coordination of the 9-keto group of ring V at one Chl (**111**) to the Mg of the next (*293*). The RC's, which are usually denoted by P (from pigment) with the appropriate indication of their electronic absorption maxima, contain special Chl complexes (*293*). In the case of PS I, the RC probably contains two Chl molecules. The absorption of the RC is shifted to the red, compared with that of the antenna Chl, and is denoted by P_{700}. Photosystem I is involved in the reduction of CO_2 by electron transfer via several "go-betweens," e.g., nicotinamide adenine dinucleotide phosphate (NADP); PS II oxidizes water to molecular oxygen. Photosystems I and II act

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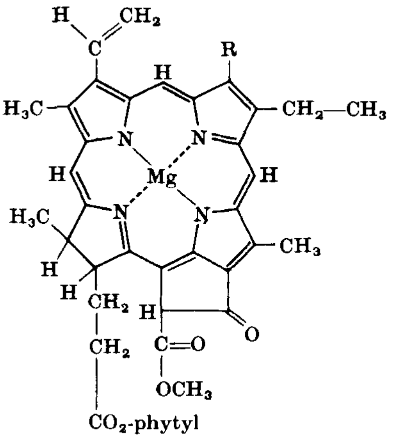
† Photosynthetic bacteria operate with a third and different system (*489*).



(R = CH_3: chlorophyll a or CHO: chlorophyll b)

(111)

in "tandem" as shown in Fig. 14 (*100*). The primary photoreaction of PS I and II can be described by the general equation

$$\mathrm{D}\cdots\ddot{\mathrm{P}}\cdots\mathrm{A} \underset{k_{-1}}{\overset{h\nu/k_1}{\rightleftharpoons}} \mathrm{D}\cdots\dot{\mathrm{P}}^{+}\cdots\mathrm{A}^{(-)} \xrightarrow{k_2} \mathrm{D}^{+}\cdots\ddot{\mathrm{P}}\cdots\mathrm{A}^{-} \tag{41}$$

where D is an electron donor and A is an acceptor. The most probable candidate for A in PS I is a bound form of ferredoxin (X in Fig. 14), since the appearance of the Chl-radical cation in P_{700} (*293*, *488*) is paralleled by the formation of a reduced form of ferredoxin (*184*, *574*, *294*). Cytochrome f and plastocyanin† have been discussed as candidates for D in PS I (*455*, *574*). The situation appears less clear for PS II, but A may be a compound related to a carotenoprotein (Q = C_{550} in Fig. 14). Cytochrome b seems to be involved as an electron donor in PS II, but not necessarily as the primary one. Evidence for the back-reaction [k_{-1} in Eq. (41)] has been obtained for PS II (*100*). So far as the complex question of the multiplicity of the excited state of Chl undergoing electron transfer is concerned, the reader is referred to Refs. *574*, *294*, *456*, and *380*.

The key role of iron-containing systems in electron transfer processes in photosynthesis can be summarized by a very crude simplification:

$$\mathrm{Chl} + \mathrm{Fe_A}^{n} \xrightarrow{h\nu} \mathrm{Chl}^{\cdot +} + \mathrm{Fe_A}^{n-1}$$

$$\mathrm{Chl}^{\cdot +} + \mathrm{Fe_D}^{n-1} \longrightarrow \mathrm{Chl} + \mathrm{Fe_D}^{n}$$

(n = oxidation state)

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† Plastocyanin is a copper-containing protein.

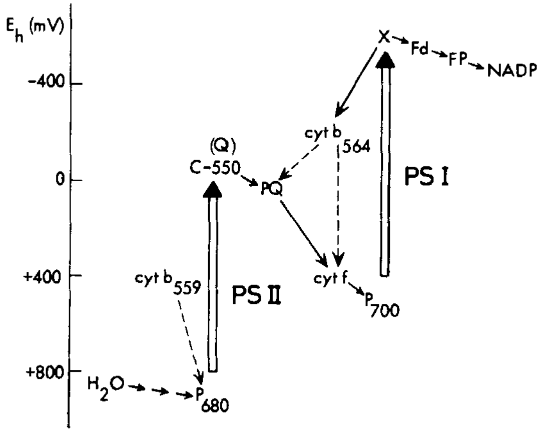


FIG. 14. Photosynthetic electron transport scheme for green plants. Dashed arrows indicate uncertain pathways. Fd = ferredoxin, FP = flavoprotein. [From Butler (*100*).]

In this context the reader should be reminded of the quenching process, involving reversible electron transfer with iron (*53*) (discussed in Section III, E, 4).

$$[\mathrm{Ru(dipy)_3}^{2+}]^* + \mathrm{Fe}^{3+} \longrightarrow [\mathrm{Ru(dipy)_3}^{3+}] + \mathrm{Fe}^{2+}$$

$$[\mathrm{Ru(dipy)_3}^{3+}] + \mathrm{Fe}^{2+} \longrightarrow [\mathrm{Ru(dipy)_3}^{2+}] + \mathrm{Fe}^{3+}$$

In general the large body of knowledge of quenching processes, involving inorganic (*28*) and organometallic compounds (*52*, *226*, *609*) should become valuable in understanding the intimate details of such processes in photosynthesis.

The iron in cytochromes is well "protected" by the porphyrin and protein (*171*) so that one wonders how electron transfer involving the iron occurs. It has been suggested (*171*) (e.g., for cytochrome c) that easily accessible portions of the porphyrin system function as the areas where electron transfer occurs and that by subsequent rapid internal transfer the iron reaches its new oxidation state:

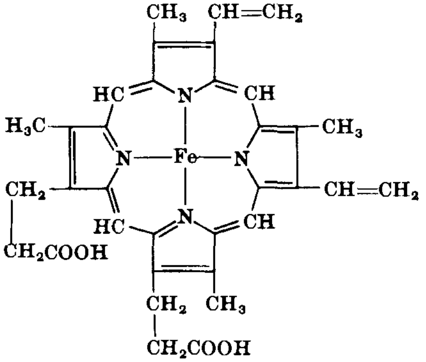
$$\mathrm{Fe(II)\ cyt\ c} \xrightarrow{-e^-} [\mathrm{Fe(II)\ cyt\ c}]^{\cdot +} \xrightarrow[\text{transfer}]{\text{internal}} [\mathrm{Fe(III)\ cyt\ c}]$$

A recent paper by Whitten *et al.* (*79*) on Ru-porphyrin complexes has demonstrated the influence of axial ligands in determining whether primary electron transfer involves the ring or the metal. We will return to this question in discussion of vitamin B_{12} photochemistry.

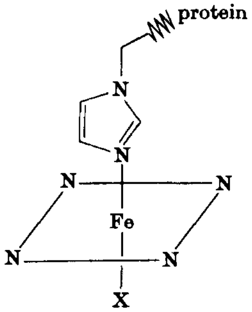
C. HEMOGLOBIN AND RELATED SYSTEMS

Direct absorption of light by porphyrin-containing transition metals does not play an important role in nature. However, the early observation by Haldane and Lorrain-Smith (*246*) of the light sensitivity of the hemoglobin–CO complex has led to detailed investigations of the photochemical behavior of a variety of hemoglobin complexes and related systems containing small molecules. These studies have led to a better understanding of details of the biological action of these systems.

The structure of hemoglobin (Hb) consists of two different pairs of subunits, each one containing a polypeptide chain and a heme (**112**) group. The chains are held together by weak interactions (hydrogen bonds, salt bridges, etc). Each heme group contains an iron atom at the center of a fully conjugated porphyrin and is bound to an imidazole N of a histidine of the polypeptide chain (**112a**). The sixth coordination site of the iron which is unoccupied in deoxyhemoglobin, can be occupied by O_2, CO, or other ligands. The formal oxidation state of the iron is II, both in oxy- and in deoxy-Hb (*15*).



(112)



(X = O_2, CO, NO, CN^-, etc.)

(112a)

Myoglobin (Mb) is a monomeric protein, consisting of a single subunit, similar in properties and structure to an Hb subunit. Its behavior is correspondingly simpler than that of Hb.

An essential property of Hb is that it is saturated with oxygen in the lungs but releases much of its oxygen in the tissues. This shift of equilibrium must occur despite relatively small differences in the concentration of O_2 between lungs and tissues. It is achieved by the interaction between the heme groups on binding oxygen: The more oxygen already bound, the more likely other oxygen molecules are to bind, until the Hb is saturated.† The mechanism of this cooperative effect has been one of the chief problems of Hb research, and an important contribution to its understanding has been made by photochemistry.

The "bioinorganochemically" minded reader, who worked himself through the section dealing with metal–CO cleavage, will now be rewarded for his endurance. The readily reversible photochemistry of HbCO allows the study of the equilibrium between liganded and unliganded forms of Hb. Gibson showed that flash photolysis of Hb could be used to observe transient species in the Hb/HbCO equilibrium (*222*). However, the interpretation of these results is complicated by the splitting of Hb into dimers, etc. (*224, 14*). Nevertheless, the method does allow the study of conformational changes if a sufficiently short time scale is used. Alpert *et al.* (*10*) have followed spectroscopic changes after laser photodissociation of CO from Hb and Mb (rate constant, ca 10^7 sec^{-1}; activation energy, ca. 1.1 kcal $mole^{-1}$). The spectra are assigned to conformational changes in the tertiary and quaternary‡ (Hb only) structures of the molecules. The pH dependence of the rate constants has been correlated with cooperativity of the proteins.

The quantum yields for ligand dissociation from heme proteins were first measured in the pioneering work of Warburg (*592, 593*). From these and later measurements (*94, 412*), it was established that the quantum yield for CO dissociation from MbCO was 0.85–1.0 and for HbCO varied from 0.25 to 0.70 according to the conditions. The greater sensitivity of HbCO than MbCO to conditions is not surprising, since Mb exhibits neither the cooperativity nor the pH sensitivity (Bohr effect) of Hb. Other Hb complexes could also be photodissociated, but the much lower quantum yields for these reactions have not been explained (e.g., $Hb—O_2{:}\Phi = 0.008$; $Mb—O_2{:}\Phi = 0.03$) (*223*).

Quantum yields have been measured not only by conventional relaxation methods (*593*) but also by steady-state (*90, 59*) and pulse methods (*91*). Steady-state illumination reduces the affinity of Hb for CO, while leaving the cooperativity and Bohr effect unaffected (*90*). The observed kinetics have been interpreted by assuming that light influences ligand binding but not the protein-modulated interactions (*554*). The pulse method (*91*) has been used to establish that the quantum yield is independent of the fractional saturation with CO and of the molecular conformation.

The structural basis of the photochemical observations have been

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† This behavior is reflected in a sigmoid O_2 binding curve (15).

‡ The folding of the individual subunits is called the tertiary structure; the relative arrangement of the subunits is the quaternary structure.

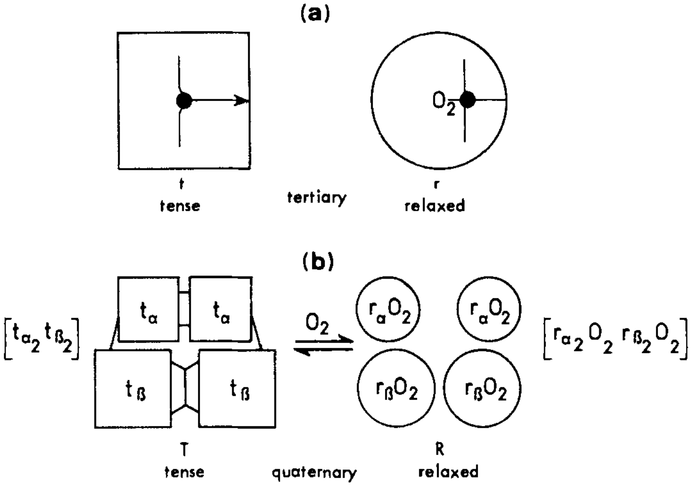


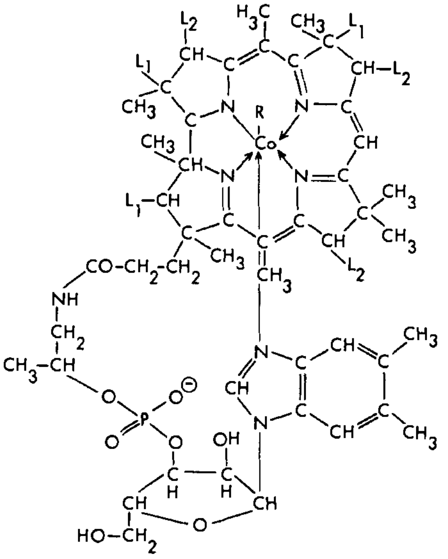
FIG. 15. (a) Diagrammatic sketch showing the relaxation of tension at the heme on going from tertiary deoxy to the oxy structure. (b) Concerted change of tertiary and quaternary structure on binding oxygen or CO to the ferrous subunits. The clamp between the β subunits in the T structure represents 2,3-diphosphoglycerate; the other links represent salt bridges. [From Perutz (*426*).]

worked out by Perutz *et al.* (*427*, *426*). They have shown by X-ray diffraction that the structures of deoxy- and oxy-Hb (or HbCO) are significantly different. In deoxy-Hb, the iron atom lies 0.65 Å out of the plane of the porphyrin ring in the direction of the histidine, whereas in HbO_2 the iron atom is close to an in-plane arrangement. The Fe—N (histidine) distance probably is longer in Hb than in HbO_2. There are also important differences in the tertiary and quaternary structure. Heme–heme interaction has been shown to be linked to a change in tension at the heme–iron atom, brought about by a transition between the two alternative quaternary structures (*263a*, *426*, *425*) (Fig. 15).

D. VITAMIN B_{12} PHOTOCHEMISTRY

After this extensive discussion of the biological applications of the principles of M—CO bond cleavage, we would like to turn to the photochemistry of vitamin B_{12} and of some model compounds as an example that demonstrates the biological relevance of homolytic M–alkyl bond cleavage (as discussed in Section IV, A, 9).

The structure of vitamin B_{12} was solved by Hodgkin *et al.* (*136*) and is shown in Fig. 16. The central cobalt atom is surrounded by the



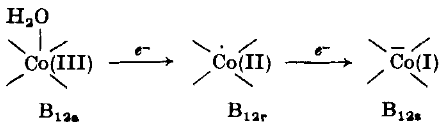
$L_1 = -CH_2-CO-NH_2$

$L_2 = -CH_2-CH_2-CO-NH_2$

$R = CN^{\ominus}$

FIG. 16. Structure of vitamin B_{12}.

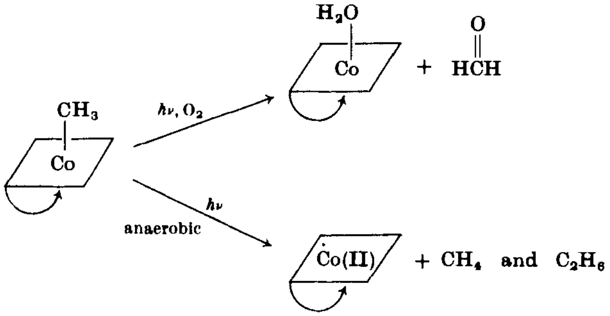
corrin ring, which is not fully conjugated. When the "lower" axial ligand is α-5,6-dimethylbenzimidazole nucleotide, the system is called *cobalamin.* The "upper" axial ligand R is variable and can be CH_3 (methylcobalamin), H_2O, OH^-, CN^- (vitamin B_{12}), 5′-deoxyadenosine, etc. The last-named compound is also called coenzyme B_{12}. The cobalt atom is normally in oxidation state III (B_{12a}) but can be reduced to oxidation state II (B_{12r}) or I (B_{12s}) (*78*):



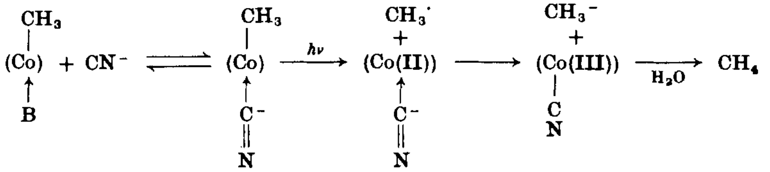
Whereas coenzyme B_{12} is a cofactor (i.e., acts in conjunction with an apoenzyme) for hydrogen-transfering enzymes, methylcobalamin is a cofactor for enzymes involved in the metabolism of one-carbon fragments. Detailed information is found in excellent reviews (*78*, *453*, *608*).

The benzimidazole side chain can be cleaved at the phosphate, leading to the cobinamide, in which H_2O normally functions as the lower axial ligand.

Methylcobalamin and related species show surprisingly high (*169*) thermal stability, but they can be readily cleaved photochemically to B_{12r} and alkyl radicals. The products of photolysis vary according to the presence or absence of O_2 (*78*). Aerobic photolysis of methylcobalamin results in the formation of formaldehyde and in photoaquation; in the absence of O_2, methane and ethane are generated:



Photolysis of CD_3–cobalamin gave 89% C_2D_6 and 11% CH_3—CD_3, indicating that the methyl groups of methylcobalamin are the main source of the ethane formed (*504*). The ratio 1:2.2 of methane to ethane in methylcobalamin photolysis can be affected by exchanging the lower axial ligand. Increase of electron density at cobalt by using CN^- as lower axial ligand results in the sole formation of methane. A mechanism involving CH_3^- formation has been proposed for this observation (*504*):



$$\begin{array}{c}CH_3\\|\\(Co)\\\uparrow\\B\end{array} + CN^- \rightleftharpoons \begin{array}{c}CH_3\\|\\(Co)\\\uparrow\\C^-\\\|\\N\end{array} \xrightarrow{h\nu} \begin{array}{c}CH_3^{\cdot}\\+\\(Co(II))\\\uparrow\\C^-\\\|\\N\end{array} \longrightarrow \begin{array}{c}CH_3^-\\+\\(Co(III))\\|\\C\\N\end{array} \xrightarrow[H_2O]{} CH_4 \qquad (42)$$

The quantum yields of methylcobalamin photolysis under oxygen are between 0.2 and 0.5, depending slightly on pH and the wavelength of incident light (*452*, *559*). Quantum yields under anaerobic conditions are much smaller; this observation has been attributed to the fast recombination of B_{12r} and the alkyl radicals formed initially. Attempts to correlate the nature of the alkyl ligand with the quantum yield of the Co—R cleavage under anaerobic conditions have to be treated with some caution, owing to the sensitivity of quantum yields toward slight traces of oxygen (*78*).

A system with an exceptional dependence on oxygen is coenzyme B_{12}, from which 8,5′-cyclic adenosine is formed at low O_2 concentrations

(*364*), and adenosine-5′-aldehyde at higher O_2 concentrations (*264*). Further information on photochemistry of B_{12}-related systems is found in Refs. *364*, *208*, *588*, *451*, *452*, *559*, *64*, *421*, *78*, *450*, and *70*.

It is generally agreed that the homolytic Co—R bond cleavage results from excitation to a R → Co CT state (note that ligand R is formally in the R^- state in the ground state):

$$\mathrm{Co(III)—R} \xrightarrow{h\nu} \mathrm{Co^{\cdot}(II)} + \mathrm{R^{\cdot}}$$

The corresponding transition has been localized in cobaloximes (see below) in the 400–450 nm area with extinction coefficients of $1\text{–}2 \times 10^3$ (*502*). It has been argued that in cobalamins this CT transition would be hidden underneath the strong intraligand π-π^* transition of the corrin π-system. Such π-π^* transitions are observed around 550 nm ($\varepsilon \sim 10^4$) and around 360 nm ($\varepsilon \sim 3 \times 10^4$) (*450*).

It appears to the reviewers as an open question whether the direct excitation of the R—Co CT band in cobalamins [suggested by Schrauzer (*502*)] would allow the relatively high quantum yields of aerobic R—Co bond cleavage to be explained. Such an assumption would demand at least unity efficiency for this process as can be seen from the ratio of extinction coefficients. In contrast to views expressed by Schrauzer (*502*), absorption of light in π-π^* transitions and internal conversion to the CT excited state, as suggested by Pratt (*450*) and Vogler (*583*), may play an important role:

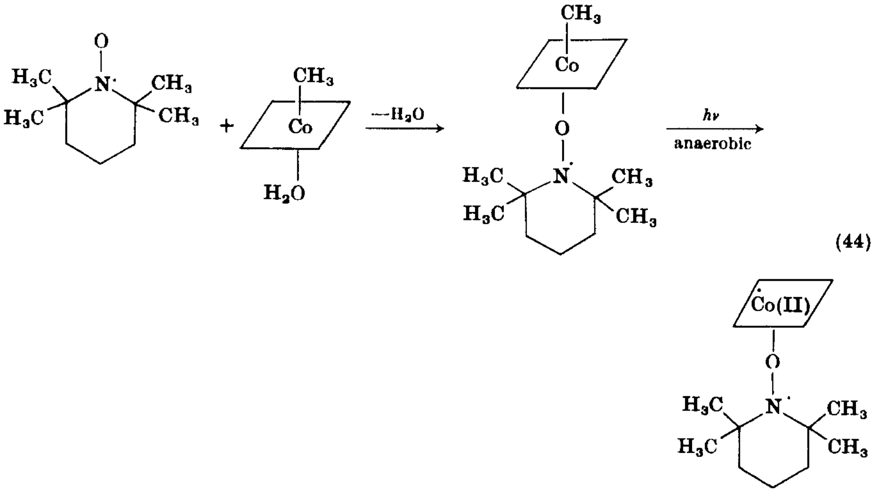
$$\mathrm{B_{12a}} \xrightarrow{h\nu} \mathrm{B_{12a}}(\pi\text{-}\pi^*) \xrightarrow[\text{conversion}]{\text{internal}} \mathrm{B_{12a}(R{\rightarrow}Co\ CT)} \longrightarrow \mathrm{B_{12r}} + \mathrm{R^{\cdot}} \qquad (43)$$

In this way the quantum yields may be simply explained. However, as will be seen from the discussion of the photoreaction of cobaloximes with oxygen (see Section V, E) the mechanistic details of the photoreaction of cobalamins with oxygen are still somewhat unclear. Arguments for internal conversion according to Eq. (43), which are based on the high values of quantum yields under aerobic conditions (*450*), are therefore still somewhat uncertain.

However, on the basis of a systematic study of the effect of different transition metals on the luminescence properties of synthetic metallocorrins, strong evidence has been produced recently that *d*-*d* states in dicyanocobalt(III)corrin are below states localized in the corrin ring system (*209a*). Only exceedingly weak fluorescence from the corrin ring is observed in this case. Strong fluorescence occurs with those metallocorrins that have *d*-*d* states, whose energy is above that of the corrin-localized states. The intramolecular quenching of emission, e.g., in the Co complex appears to be a reliable criterion for internal conversion to *d-d* states, from which chemical reactions at the metal center may originate (*209a*).

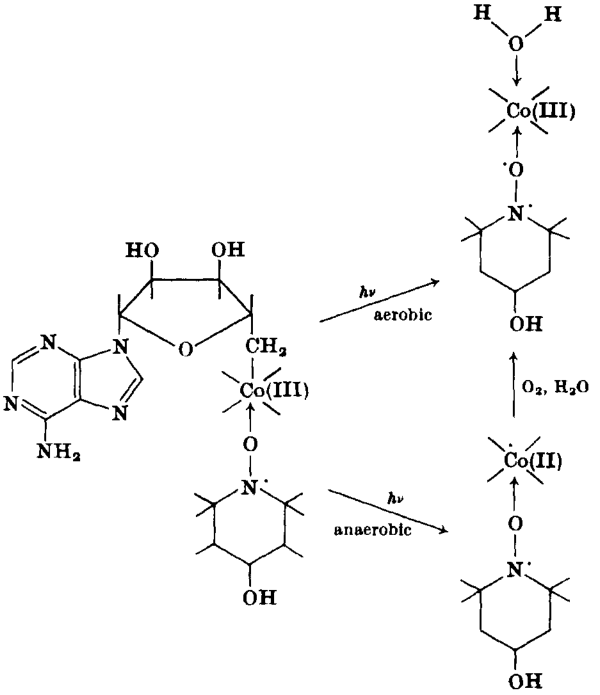
The extent to which internal conversion occurs from π-π^* states in cobalamins to *d-d* states in competition with the R—Co CT state remains unclear. Final clarification of this point appears all the more desirable since the major biological application of B_{12} photochemistry has been to examine the involvement of radicals in enzymatic reactions. Existing or missing parallels between enzymic reactions and the photochemical behavior of cobalamins and cobaloximes toward model substrates have been used as guidelines to argue for or against radicals as enzymic intermediates (*78*, *506*). A typical example is the controversial discussion about the mechanism of action of coenzyme B_{12} in dioldehydrase and related systems (*78*, *503*, *531*, *81*).

It should be pointed out that another very significant method for investigating the oxidation state of cobalt in enzymic reactions is that of "spin labeling" by introduction of nitroxyl radicals (*78*). As a typical example the formation of labeled cobinamide is shown:



(44)

Aerobic photolysis of the methyl(nitroxide)cobinamide produces the aquo(nitroxide)cobinamide according to ESR evidence. However, anaerobic photolysis generates the cobalt(II) compound [Eq. (44)]. Similar results have been obtained with spin-labeled cobinamide coenzyme (Scheme 3). The cobalt(II) species does not give any ESR signal, probably owing to spin pairing of the two odd electrons (*363*). Admission of oxygen regenerates the signal of Co(III) (as aquo complex) completely.



(45)

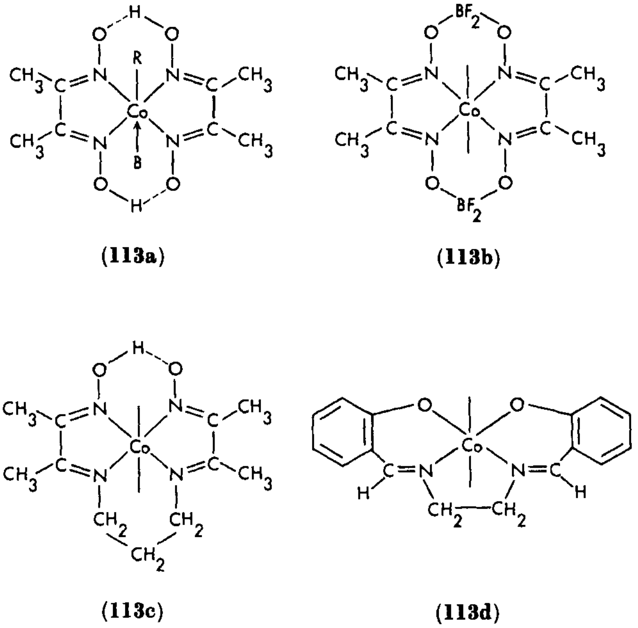
Scheme 3

E. Photochemistry of Cobaloximes

One of the most exciting aspects of B_{12} photochemistry (and chemistry in general) is that much of it can be studied using relatively simple molecules as models. Some of these model complexes are listed in Fig. 17.

The "equatorial" corrin system of B_{12} is replaced in most of these model complexes by the bis(dimethylglyoximato) (*499*) or, less frequently, by bis(salicylideneiminato) system (*48*) and derivatives thereof (*169*). It was convincingly demonstrated by Schrauzer (*499, 500, 502*) on the basis of its analogous chemical reactions, spectra, and electronic structure (derived from EHMO calculations) that the properties of cobalt(III)bis(dimethylglyoximato) complexes of the general structure (**113a**) very closely resemble those of cobalamins. They have therefore been named cobaloximes.

The photochemistry of cobaloximes (*169*) also parallels that of cobalamins (*78, 502, 504, 505*). However, the quantum yields for Co—R cleavage under aerobic conditions are smaller by a factor of 10

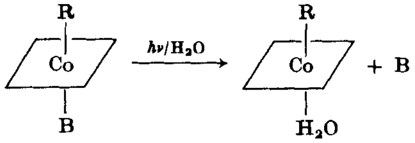


(113a) **(113b)**

(113c) **(113d)**

FIG. 17. Inorganic model systems for B_{12}: (**113a**) bis(dimethylglyoxime) cobalt (or cobaloxime) with axial alkyl (R) and base (B) ligands; (**113b**) BF_2–cobaloxime; (**113c**) diacetylmonoximeiminodiacetylmonoximatoiminopropane 1,3-cobalt; (**113d**) *N*, *N*′-ethylenebis(salicylideneiminato)cobalt. [From Brown (*78*).]

for the cobaloximes (*502*). The wavelength of irradiation was in the 400–450 nm region; the electronic spectra of cobaloximes show an absorption maximum in this region, which has been attributed to an alkyl-to-cobalt charge transfer (*502*). It has been argued that the difference in quantum yields is due to the lower strength of the Co—C bond in cobalamins as compared with the cobaloximes.† Photodissociation of the bond between cobalt and the lower axial ligand B appears to be an important process in cobaloxime photochemistry, according to recent observations by Giannotti *et al.* (*216*) (under aerobic conditions):



(46)

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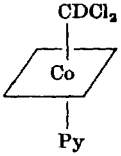
† "A slightly greater partial positive charge on cobalt" in the cobaloximes in comparison to the cobalamins, as derived from EHMO calculations, has been correlated with "slightly more stable" axial bonds in the cobaloximes (*502*).

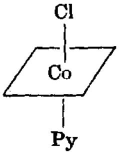
Another explanation could be a different ratio of photodealkylation and cleavage of the Co—B bond in cobaloximes and cobalamins, due to different rates of internal conversion processes.

How complicated it may be to discover the detailed mechanism of B_{12} photodealkylation becomes obvious from a recent ESR study of anaerobic alkylcobaloxime photochemistry (*214*). Of the cobaloximes investigated which all contained pyridine as lower axial ligand B, those with R = methyl and benzyl abstracted an electron from the solvent ($CHCl_3$ with $\sim 0.75\%$ C_2H_5OH at $-20°C$) in the primary photochemical process, leading to a Co(II) species still containing both axial ligands. On the other hand, the cobaloximes with R = isopropyl, isobutyl, *n*-pentyl, and cyclohexyl at $-160°C$ gave the corresponding radicals R and the dealkylated Co(II) species. On warming up the samples to $-100°C$ further changes occurred, which were ascribed to "loss of the pryidine ligand or substitution of a solvent molecule in the alkyl position." This work provides the first direct evidence for the production of cobalt(II) species as the primary products of anaerobic cobaloxime photochemistry. However, it should be noted, that the formation of (**114**) and (**115**) results from anaerobic irradiation of cyclohexylpyridinatocobaloxime in $CDCl_3$ (*173*).



(**114**)

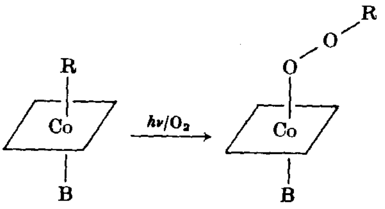
and



(**115**)

The effect of R on the course of photolysis resembles observations by Schrauzer (*502*): The photolysis rates of alkylcobaloximes increased in the order $CH_3 < C_2H_5 < CH_2CH(CH_3)_2 < C_6H_{11}$.

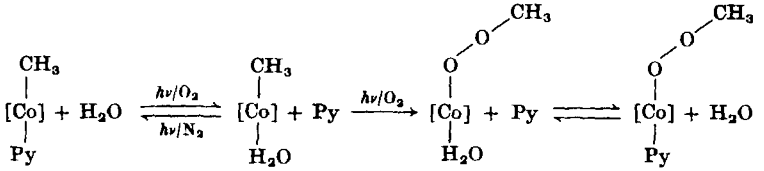
The aerobic photochemistry of cobaloximes confronts us with another set of problems. In a series of papers it was shown by Giannotti and his collaborators (*219*, *174*, *205*, *221*, *381*, *216*) that alkylperoxycobaloximes (**116**) can be isolated from the photoreaction (in the range of $-20°$ to $120°C$) of alkylcobaloximes with O_2:



(**116**)

For R = $-CH(CH_3)(C_6H_4CH_3)$, the structure was confirmed by X-ray diffraction (*113*). Benzyl- and allylcobaloximes also produced **116** in a thermal reaction at ambient or slightly elevated temperatures (*174*). Anaerobic decomposition of compound **116** by further irradiation or heating gave alcohols, aldehydes, and/or ketones depending on the solvent and R (*215*).

Since similar peroxy compounds could play a role in the aerobic cobalamin photolysis (see section V, D), the mechanism of alkylperoxycobaloxime formation deserves special interest. The following scheme has been proposed recently for methylcobaloxime (*216*):



$$\underset{Py}{\overset{CH_3}{[Co]}} + H_2O \xrightleftharpoons[h\nu/N_2]{h\nu/O_2} \underset{H_2O}{\overset{CH_3}{[Co]}} + Py \xrightarrow{h\nu/O_2} \underset{H_2O}{\overset{O-O-CH_3}{[Co]}} + Py \rightleftharpoons \underset{Py}{\overset{O-O-CH_3}{[Co]}} + H_2O \qquad (47)$$

The first detectable photochemical reaction of alkylcobaloximes (in alcoholic solution) in the presence of water generally appears to be the expulsion of the lower axial ligand B and the rapid formation of the alkyl(aquo)cobaloxime (*216*), as demonstrated for a variety of B species, including spin-labeled amines (*221*, *216*)† The insertion of O_2 into the Co—R bond of the aquo complex needs another light quantum. The suitability of the aquocomplex for this second step parallels the general enhancement of relative aerobic photolysis rates of alkylcobaloximes on decreasing the basicity of B, rendering the aquo complexes the most photoreactive systems (*502*). This phenomenon may be owing to a favorable ratio of internal conversion leading to Co—R cleavage, as compared with that leading to ligand (e.g., B) expulsion and other processes.

The effect of water as axial ligand can be rationalized using a very simplified MO picture (Fig. 18). Let us consider for the axial bonding of B and R in cobaloximes only the cobalt $3d_{z^2}$ and $4p_z$ and the R and B σ-orbitals. In the first step we produce a symmetric and an antisymmetric combination by letting the two σ-orbitals interact. The energy and composition of the two linear combinations will be quite different, according to whether the interaction is weak (Fig. 18A) or strong (Fig. 18B). Whereas in the former case the transition $\sigma_2 \rightarrow \sigma_3^*$ has substantial $CH_3 \rightarrow Co$ charge-transfer character, this action is

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† Apparently, it has only been demonstrated that photoaquation *precedes* O_2 insertion under aerobic conditions in the case of methylcobaloxime.

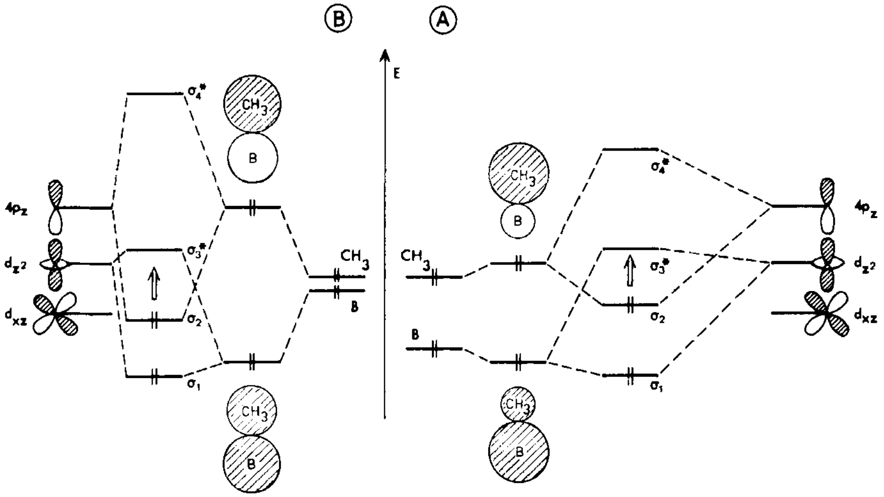
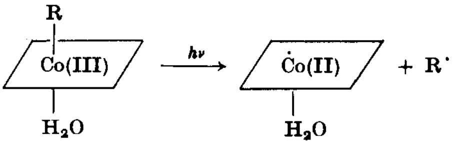


FIG. 18. Simplified MO scheme demonstrating the interaction among CH_3, base B, and cobalt orbitals for (A) weak interaction of CH_3 and B and for (B) strong interaction of CH_3 and B in cobaloximes.

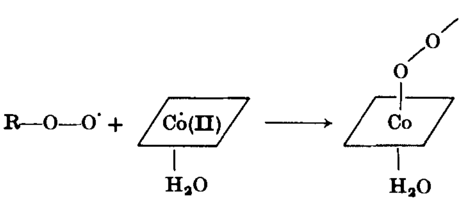
somewhat reduced in the latter case. Thus, with weak interaction and B = H_2O (I.P., 12.6 eV), formation of $CH_3\cdot$ would be more probable, but with strong interaction and B = pyridine (I.P., 9.3 eV), less reaction resulting from homolytic Co—CH_3 cleavage and more dissociation of the Co–pyridine bond (as well as of Co—$CH_3 \rightarrow Co^+ + CH_3^-$) would be expected. In addition, it is not obvious whether *d-d* transitions would become more important if the CT-transition energy is raised somewhat (Fig. 18B); e.g., $d_{xz} \rightarrow d_{z^2}$ may come into play in this case, especially if pyridine, for instance, shifted MO's with strong d_{xz} contribution by π-interaction. Excitation of $d_{xz} \rightarrow d_{z^2}$ transition would increase the repulsion between Co and R and B, thus accelerating, for instance, photoaquation.

In the case of a CT process preceding O_2 insertion, the overall reaction would be as follows:



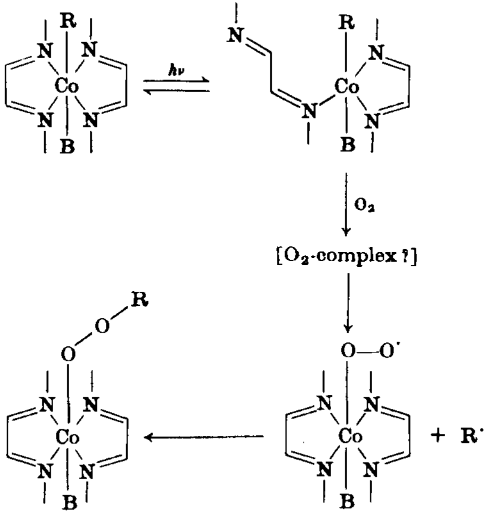
$$\underset{H_2O}{\overset{R}{\boxed{Co(III)}}} \xrightarrow{h\nu} \underset{H_2O}{\boxed{\dot{C}o(II)}} + R^{\cdot} \qquad (48)$$

$$R^{\cdot} + O_2 \longrightarrow R{-}O{-}O^{\cdot} \qquad (49)$$



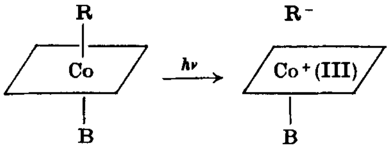
(50)

Since substantial quantum yields for Co—R cleavage in cobalamins (*450*) as well as cobaloximes (*502*) can only be observed under aerobic conditions, we have no direct information whether all or only a fraction of Co—OO—R is formed according to the mechanism shown in Eqs. (48)–(50). In order to challenge investigators in this field to produce more quantitative data, the reviewers would like to suggest two further



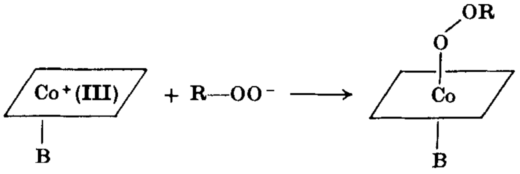
SCHEME 4

mechanisms for the formation of Co—OO—R (Scheme 4). Photochemically triggered partial decoordination of one "equatorial" nitrogen (e.g., as a result of a d_{xz} or $d_{yz} \rightarrow d_{x^2-y^2}$ transition)[†] could allow an attack of O_2 on Co, resulting in the formation of a radical pair and its subsequent combination as follows:



[†] The fast back-coordination of the nitrogen in the absence of oxygen could be a very efficient pathway of radiationless deactivation.

$$R^- + O_2 \longrightarrow R{-}OO^-$$

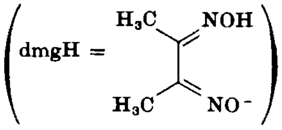


Dissociation of a Co—R bond to Co^+ and R^- (as a result of a *d-d* excitation or electron transfer, see page 70) with concomitant attack of O_2 on R^- and combination of the two ionic species could also lead to the peroxy compound. Note that the high basicity of B leads to exclusive formation of CH_4 from Co—CH_3 (via CH_3^- + H_2O) (*504*), and also supports photodissociation into Co^+ + R^-, according to Fig. 18B.

This mechanism would not be important for aquo complexes. In protic media, alkane formation would compete with oxygen insertion.

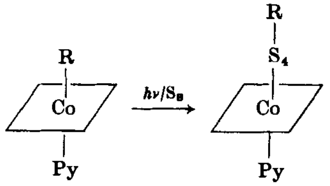
As a third alternative mechanism, one suggested by Dodd and Johnson (*169*), should be considered:

$$\mathrm{RCo(dmgH)_2py} \xrightarrow{h\nu} \mathrm{RCo(dmgH)_2 + py}$$
$$\mathrm{RCo(dmgH)_2 + O_2} \rightleftharpoons \mathrm{RCo(dmgH)_2OO\cdot}\ \text{(cis ?)}$$
$$\mathrm{RCo(dmgH)_2OO\cdot + py} \longrightarrow \mathrm{ROO\ Co(dmgH)_2py}$$

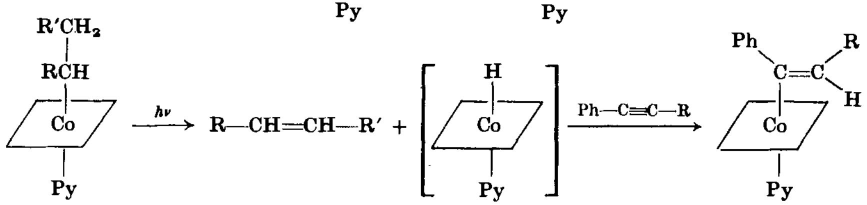


Although, in general, preference is given to a radical mechanism for the formation of alkylperoxycobaloximes (*381*, *216*), attempts to find chemical evidence for the ionic or radical character of R in the course of reaction failed to give an unequivocal answer (*381*). The stereochemistry of R in the reaction with O_2 is also a controversial issue. Although in some cases compounds with optically-active carbon attached to cobalt did not racemize in the insertion reaction (*205*, *218*), complete racemization was observed with other systems (*282*). Whether these discrepancies are due to "ghost" rotations of the highly colored solutions that are opaque to light (*282*) or due to a difference in reaction mechanism remains obscure.

Other interesting photoreactions of alkylcobaloximes which we would like to mention, are the photochemical insertion of sulfur (*217*) and the β-elimination of olefins (*173*) observed in the anaerobic photolysis of cobaloximes:



(51)



(52)

Summaries of the literature concerning the photochemistry of other "model" complexes are found in Refs. *124*, *125*, and *117*.

In summing up, it can be stated that the photochemistry of vitamin B_{12} model complexes is an extremely exciting and active field. Two factors have been of special importance: (a) The close relationship in chemistry and spectroscopy between "model" systems and the "real" B_{12} is an ideal situation for fruitful cooperation among inorganic, organometallic, photo-, and biochemistry; and (b) The environmental "mercury" problem, which is caused by the alkylation of mercury by B_{12} (*78*), has led to much (hopefully long-lasting) attention for this field of biochemistry.

However, we should not close this section without a quotation from D. G. Brown (*78*): "The inorganic chemist has profited more from B_{12} than B_{12} has profited from him!" Much remains to be done!

VI. Conclusions

Photochemistry is now well-established as one of the important techniques in the arsenal of the organometallic chemist. This is especially true of the preparative field, as is demonstrated by the numerous photochemical syntheses and transformations of organometallic compounds.

The possibility of working at low temperatures opens up a route to thermally unstable compounds. The preparation of catalytically active compounds and the clarification of reaction mechanisms by synthetic and/or spectroscopic identification of intermediates are two important applications of the low-temperature techniques.

The knowledge of primary processes in organometallic photochemistry has greatly increased in recent years. For instance, it provides useful information about the structure and reactivity of coordinatively unsaturated species, about energy transfer, and about the connection between electronic excitation and chemical reactivity. The knowledge gained from model compounds will surely be used more extensively in understanding the more complicated systems, in particular for bioinorganic species.

There are many contacts between organometallic photochemistry and areas of "conventional" chemistry, biology, medicine, and technology. A few examples should give an idea of the varied possibilities.

The photochemical reactivity of organometallic systems is subtly dependent on small changes in the conditions. For instance, the dramatic effect of a change of substitutents on the ratio of internal conversion to chemical reaction provides a challenging exercise for the theoretician. The theoretical understanding of radiationless processes in transition metal complexes (*472a*) will have particular importance in the future.

Application of laser radiation in organometallic photochemistry is as yet little explored. There are already some examples of the preparative use of intensity-dependent reactions (*613*). In addition the application of lasers will give new stimulus to the partial photoresolution of racemates of transition metal compounds (*487a, 626a*).

At a time when the use of solar energy is receiving so much attention (*250*), it is essential to have a better understanding of the role that bioinorganic compounds play in the collection, transmission, and chemical conversion of solar energy.

The application of photochemistry to organic synthesis has been furthered by the use of transition metals. The introduction of transition metals allows particular spatial configurations to be fixed by coordination of transition metals to selected centers. In this way photochemical bond formation is rendered possible between centers whose approach is normally highly improbable. An outstanding example is the final ring closure in Eschenmoser's (*626a*) corrin synthesis which was achieved by the photochemical cycloisomerization of the secocorrinoidic palladium complex involving a 1,16-hydrogen shift. Luminescence studies have decisively demonstrated the reasons for the effects of different transition metals on this reaction (*209a*).

Metalloporphyrins are interesting catalysts for the activation of C—H bonds in organic substrates (*422a*). The application of photochemistry to this problem also has great promise.

Apart from preparative applications, organometallic photochemistry should be of industrial use in "imaging" processes. The initiation of polymerization reactions is being extensively investigated (*29, 417a, 552a*). The potentially useful association of color changes with changes in electrical properties in organometallic photoreactions has not yet found major application in data fixation.

In the area of photobiology the effect of the coordination of heavy metals on DNA should be mentioned as well as the use of model compounds. The different effects of Ag^+ and Hg^{2+} on the photoinactivation of DNA (and on thymine dimerization) pose interesting questions about the role of transition metals in radiation damage.

The discovery that transition metal complexes, such as *cis*-$Pt(NH_3)_2Cl_2$, have useful properties as antitumor drugs will stimulate research on the mechanism of interaction of such complexes with model compounds of important cell components (*559a*). In the case of $Pt(NH_3)_2Cl_2$, only the cis and not the trans complex is effective; the photochemical cis-trans photoisomerization may be useful in this connection.

The wide range of sources for this article makes it appropriate to quote a saying of Edward John Phelps found in a recent book on photochemistry (*534*): "The man who makes no mistakes usually does not make anything." This principle has allowed us to infringe an old Latin proverb: *O si tacuisses, philosophus manisisses!*

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