# PHOTOCHEMISTRY OF CARBONYL COMPLEXES

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### I. INTRODUCTION

The photosensitivity of metal carbonyls has been known almost as long as the class of coordination compounds itself. Among no other group of inorganic compounds may one find so many light-sensitive materials. Hence photochemical reactions of metal carbonyls have found wide applications for synthetic purposes. However, whereas much research has been done to understand the thermal reactions,[1-3] the mechanism leading to photochemical reactions of metal carbonyls is not yet well investigated. The papers that have appeared on the photochemistry of metal carbonyls are largely restricted to preparative aspects, although some preliminary attempts have been made to correlate the photochemical reaction with the electronic structure of these compounds. Two excellent reviews of the photochemistry of metal carbonyls are of special importance.[4,5] In 1964 the first review was published by Strohmeier,[6] who did pioneering work in this field, and in 1969 von Gustorf and Grevels presented a comprehensive survey on this subject.[7] During the last few years considerable progress has been made, particularly in the investigation of primary photochemical steps. However, the lack of sufficient information on the complicated electronic structures of metal carbonyls remains an obstacle to the understanding of their photochemical reactions.

Since the metal in most carbonyl complexes, such as $Cr(CO)_6$, has the formal oxidation state, zero, a simple electrostatic picture can not account for the stability of these compounds. Only MO theory provides a model that is in agreement with the chemical and physical properties of metal

carbonyls. The necessary condition to form a stable complex with a metal in a low oxidation state is that the ligands be able to form $\pi$ acceptor bonds in addition to $\sigma$ donor bonds. The ligands must provide empty $\pi$ orbitals that are low enough to interact with lower lying filled $d\pi$ orbitals of the metal. The occupied, nonbonding $d\pi$ orbitals are thus lowered in energy to give $\pi$-bonding MOs that contribute very much to the stability of the complex. The metal character of this $\pi$-bonding MO may still predominate, but some electron density of the metal is shifted toward the ligands. The extension of the metal $d$ orbitals toward the ligands thus introduces an appreciable covalent character into the metal-ligand bond. This delocalization of $d$-electron density into the ligands induces an electrostatic attraction between ligands and metal. It follows that the formation of $\pi$ acceptor bonds ("back donation" of charge), in turn, facilitates increased $\sigma$-bonding, which again contributes to the stability of the complex. Both effects, $\pi$- and $\sigma$-bonding, are responsible for the very large $d$ orbital splittings that occur in metal carbonyls.

It is generally accepted that this picture describes the bonding situation of metal carbonyls qualitatively. However, the quantitative description is still controversial among investigators in this field. Although different semiempirical MO calculations seem to agree with the experimental data obtained for a certain metal carbonyl, the detailed interpretation of the nature of the bonding varies with the calculational procedure used. For a critical survey of the different methods and their limitations the reader is referred to a paper by Fenske.[8]

Photoelectron spectroscopy provides a good tool to determine the origin and the energies of the occupied MOs; ground electronic states are fairly well described. Much less reliable information is available on the empty MOs. The large $d$ orbital splittings and the introduction of low-lying antibonding $\pi^*(CO)$ states of different symmetries lead to an accumulation of many empty MOs in a narrow energy range compared to complexes with $\sigma$-bonding ligands only. It follows that the absorption spectra are ill resolved because many electronic transitions give rise to absorption bands in the same wavelength region. Weak bands may not be identified at all. None of the absorption spectra of metal carbonyls show well-separated ligand-field bands. In addition, the intensity criterion for the distinction between LF and CT bands may not work very well because Laporte forbidden transitions may become more allowed in metal carbonyls due to very effective vibronic coupling with allowed transitions as a consequence of the strong covalent interaction between ligand and metal. In any case, many reasonable assignments of absorption bands of metal carbonyls were made by the application of temperature- and solvent-dependent absorption spectroscopy and spectroscopy with polarized light on the basis of selection rules and similar restrictions. In

particular, the work of H. B. Gray has contributed much to the understanding of the electronic spectra of metal carbonyls.

Very little information is available on the photophysical processes following light absorption. Emission spectra have been obtained only for a few substituted metal carbonyls. It does seem that higher excited states of metal carbonyls are deactivated to the lowest excited state as the precursor of a photochemical reaction since, in some important cases, the quantum yield has been shown to be wavelength independent. The deactivation of higher excited states may be facilitated by the strong interaction of states of different origin and symmetry. Hence our discussion of excited states is largely confined to the lowest excited states of metal carbonyls. This restriction is also justified by the fact that most of the photochemical work is limited to the irradiation of the long-wavelength bands of metal carbonyls. In the following sections, an attempt is made to explain the photochemical reactions of metal carbonyls on the basis of the nature of those excited states that may initiate the observed photoreactions. Hence many interesting photochemical reactions are not mentioned here if the available information is not sufficient to allow a meaningful conclusion or at least a reasonable speculation about the mechanism of a photochemical reaction. The reader is referred to the reviews cited above if he is interested only in preparative aspects of the photochemistry of metal carbonyls.

## II. HEXACARBONYLS OF CHROMIUM, MOLYBDENUM, AND TUNGSTEN

Upon irradiation of $M(CO)_6$ (M = Cr, Mo, W) dissolved in organic solvents, the release of one CO ligand is observed. The mechanism of this reaction may be closely related to that of the photochemical substitution of one $CN^-$ group upon irradiation of the isoelectronic $Co(CN)_6^{3-}$ in aqueous solutions.[9] The photoactive excited state of $Co(CN)_6^{3-}$ was shown to be of the ligand-field type since the photochemical reaction was produced upon irradiation of the LF bands that are well separated from and lower in energy than the lowest CT bands. But the photoactive LF state is probably not the singlet that is reached directly by a spin-allowed transition from the ground state. The lowest LF triplet state that may be populated by intersystem crossing seems to be the precursor of the photoaquation; this state was shown to be the active one for the sensitized photolysis of $Co(CN)_6^{3-}$.[10]

### A. Electronic Structure

$Co(CN)_6^{3-}$ and $M(CO)_6$ are both octahedral complexes with six $d$ electrons at the central metal. Carbon monoxide and $CN^-$ are both ligands that are

able to form $\pi$ acceptor bonds. But the extent of $\pi$-bonding and hence of electron delocalization is much larger for $M(CO)_6$ due to the low oxidation state of M and the better $\pi$ acceptor properties of CO. It is thus not surprising that the electronic structures of $Co(CN)_6^{3-}$ and $M(CO)_6$ differ in some important details.[11] The influence of $\pi$-bonding in $M(CO)_6$ is shown in a simplified MO scheme (Fig. 6-1).

Photoelectron spectra show that the highest occupied orbitals of $M(CO)_6$ are $\pi$-bonding $t_{2g}$ orbitals.[13] These $t_{2g}$ orbitals are assumed to be composed of 75% $d_{xy}$, $d_{yz}$, $d_{xz}$ and 25% $\pi^*(CO)$ orbitals in the case of $Cr(CO)_6$.[14] The absorption spectra of $M(CO)_6$ species[15] exhibit two intense bands at around 35,000 cm$^{-1}$ and 44,000 cm$^{-1}$. Most importantly, the first band is unsymmetric and shows some structure on the low-energy tail. The close spacing and small resolution of these shoulders have made assignments quite difficult.

A detailed interpretation of the $M(CO)_6$ spectra was given by Beach and Gray.[15] The long-wavelength shoulder of $W(CO)_6$ and $Mo(CO)_6$ was assigned to the lowest spin-forbidden ($^1A_{1g} \rightarrow {}^3T_{1g}$) LF transition. A similar assignment of a weak long-wavelength absorption of $Cr(CO)_6$ was made in an older study.[16] The next two shoulders were attributed as vibrational structure of the lowest spin-allowed ($^1A_{1g} \rightarrow {}^1T_{1g}$) LF transition ($t_{2g} \rightarrow e_g$ in Fig. 6-1). Both intense bands, around 35,000 cm$^{-1}$ and 44,000 cm$^{-1}$, were assigned to symmetry- and spin-allowed CT transitions of the metal-to-ligand $t_{2g} \rightarrow \pi^*(CO)$ type. However, the position of the band maximum near 35,000 cm$^{-1}$ was almost solvent independent, whereas the band near 44,000 cm$^{-1}$ showed a solvent-dependent shift. In addition, the solvent-dependent band was about ten times as intense as the other one. These facts were taken as evidence that the band near
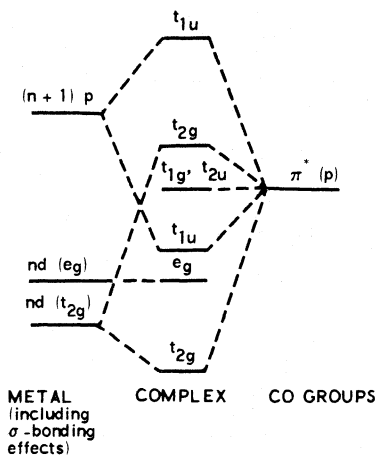


METAL
(including
$\sigma$-bonding
effects)    COMPLEX    CO GROUPS

**Fig. 6-1.** Simplified molecular orbital diagram for typical $M(CO)_6$ complex.

35,000 cm$^{-1}$ belongs to the $t_{2g} \rightarrow t_{1u}$ CT transition; this transition is not a complete electron transfer since the $t_{1u}\pi^*(CO)$ orbital is not a pure ligand orbital due to the admixture of metal character. The more intense band around 44,000 cm$^{-1}$ was assigned to the $t_{2g} \rightarrow t_{2u}$ CT transition. This transition is associated with an almost complete electron transfer to the ligand since the $t_{2u}$ orbital is a $\pi^*(CO)$ orbital that does not interact with metal orbitals. The other possible low-energy $t_{2g} \rightarrow \pi^*(CO)$ CT transitions are symmetry forbidden. Their absorption bands are difficult to identify. It should be mentioned here that different assignments were made by Schreiner and Brown.[17] These authors calculated the $t_{2u}$ orbital as the lowest empty MO. According to this assumption, the longest wavelength absorption of Cr(CO)$_6$ was assigned to the $t_{2g} \rightarrow t_{2u}$ CT transition.

## B.   Photochemical Behavior

The quantum yield for the photodissociation of M(CO)$_6$ to M(CO)$_5$ and CO was found to be unity and independent of the solvent.[6,18] It seems likely that the excitation of higher CT states leads to a complete internal conversion to the lowest excited state as the precursor of the photochemical reaction. Since the lowest excited state is assumed to be a LF state, the release of a CO ligand may be caused by the labilization of the M—CO bond that occurs if an electron is removed from bonding $d\pi$ orbitals and added to antibonding $d\sigma$ orbitals. This assumption is supported by another observation. Evidence was obtained that the reduction of M(CO)$_6$ by sodium, which should lead to an occupation of the antibonding $e_g$ orbitals, causes a labilization of M(CO)$_6$ and the subsequent formation of [M(CO)$_5$]$^-$.[19] The internal conversion from higher CT states to the lowest LF state, a process that is not common for the metal ammines,[4,5] may be facilitated by the strong mixing of LF and CT states. In analogy to Co(CN)$_6^{3-}$, the photoactive excited state of M(CO)$_6$ may be expected to be the lowest excited LF triplet. In a sensitized photoreaction in benzene it was shown that the energy of the lowest excited triplet of benzophenone can be transferred to the lowest triplet of Cr(CO)$_6$,[20] which then undergoes the well-known photodissociation with a limiting quantum yield of one. It was assumed that the direct or unsensitized photolysis also originates from this triplet state, which may be reached via intersystem crossing from excited singlet states.

The absence of any photoredox reaction upon CT excitation of M(CO)$_6$ may be taken as evidence for the complete internal conversion to the lowest excited LF state as precursor for the photochemical release of CO. However, in the case of Ni(CO)$_4$ (see below), it can be shown that the release of CO must be initiated by a metal-to-CO CT excited state. Hence

the possibility that CT excitation of $M(CO)_6$ leads directly to the observed photochemical reaction cannot be excluded at present. In the lowest $d\pi$ to $\pi^*(CO)$ CT transition ($t_{2g} \rightarrow t_{1u}$) no extensive charge separation is achieved due to the large degree of electron delocalization. The photodissociation may simply occur because an electron is transferred from a $\pi$-bonding to a $\pi$-antibonding MO of $M(CO)_6$. Irradiation of the very intense and solvent-dependent band near 44,000 cm$^{-1}$, which corresponds to a CT transition from a $d\pi$ to a noninteracting $\pi^*(CO)$ orbital, also leads to the release of CO.[21] The behavior may be due to the deactivation of this excited state to lower ones which initiate the photodissociation, since the transfer of an electron to an noninteracting $\pi^*(CO)$ orbital should not labilize M—CO bonds. Photoelectron production that might be expected to occur upon irradiation of the solvent-dependent band is not likely to be observed, according to rules of Waltz and Adamson.[22]

The nature of the $M(CO)_5$ fragment produced in the primary step of the photolysis of $M(CO)_6$ has been investigated extensively. Strohmeier, in the early 1960s, studied the photodissociation of $M(CO)_6$ to give $M(CO)_5$ and CO.[23] A thermal back-reaction may regenerate $M(CO)_6$. However, in the presence of a potential ligand, L, the $M(CO)_5$ fragment can react with L to yield stable $M(CO)_5L$. Irradiation of $M(CO)_6$ in isopentane methylcyclohexane/glasses at 77°K gave a new species that was assumed to be $M(CO)_5$.[24] Infrared data were consistent with a $C_{4v}$ square pyramidal structure of this fragment. Slow warming led to a structure change of $C_{4v}$ $M(CO)_5$ at the softening point of the glass. According to infrared measurements, a $D_{3h}$ trigonal bipyramidal $M(CO)_5$ was formed. On further warming the solution became fluid, and $M(CO)_5$ recombined with the released CO to regenerate $M(CO)_6$. The photolysis of $M(CO)_6$ is accompanied by a reversible change from colorless to yellow, reversed in the thermal back-reaction. This photochromic behavior was demonstrated with $Cr(CO)_6$ dissolved in methyl methacrylate polymers[25] and investigated by flash photolysis of $Cr(CO)_6$ in fluid solutions and polymers.[26]

In contrast to the above results it was shown only recently that even at low temperatures in rigid media an isolated $C_{4v}$ $M(CO)_5$ fragment probably does not exist.[17,21,28] One of the molecules in the medium is assumed to fill the coordination gap. Since any molecule present in the solvent or matrix cage of $M(CO)_6$ may photosubstitute one CO ligand, it was suggested that the released CO escapes from the solvent cage. The absorption spectrum and the stability of $M(CO)_5A$, where A denotes a medium molecule, varies with the ligand properties of A. If $M(CO)_6$ was photolyzed in methyltetrahydrofurane (MTHF) glass at 90°K, $M(CO)_5$MTHF was formed.[28] On melting the glass no immediate change

occurred since MTHF is a moderately good ligand. On further standing a slow regeneration of M(CO)₆ took place.

In a series of very sophisticated experiments, J. J. Turner and co-workers studied the photolysis products of M(CO)₆ in gas matrices at low temperatures.[21,27,29] In an argon matrix a M(CO)₅ species was formed. Its infrared spectrum was consistent with a square pyramidal structure. In the case of chromium the M(CO)₅ fragment exhibited a long-wavelength absorption at 542 nm. The interaction of M(CO)₅ with an argon atom that may fill the coordination sphere to give M(CO)₅Ar must be very small due to the negligible coordinating ability of an inert gas. With increasing interaction in other media the long-wavelength absorption of M(CO)₅ was shifted to higher energies. Interestingly, the absorption spectra of photolyzed Cr(CO)₆ in an alkane glass ($\lambda_{max}$ = 485 nm) and in a methane matrix ($\lambda_{max}$ = 492) were very similar. The comparison of the spectra of Cr(CO)₅ in argon and methane matrices indicates a considerable interaction between methane and Cr(CO)₅. The existence of Cr(CO)₅CH₄, which, however, is stable only at low temperatures, may not be too surprising since stable transition-metal complexes with $BH_4^-$ as ligand are well known[30]; $BH_4^-$ is isoelectronic with CH₄. Evidence for the formation of M(CO)₅N₂ was found if M(CO)₆ was photolyzed in a nitrogen matrix at low temperatures.[21] If W(CO)₆ was photolyzed at 20°K in an argon matrix doped with C¹⁸O, two products were formed: a W(CO)₅ fragment identical with that obtained in pure argon and W(CO)₅(C¹⁸O). All these experiments provide sufficient evidence that any molecule present in the solvent cage of M(CO)₆ may fill the coordination gap of M(CO)₅. It follows that the released CO should have enough kinetic energy to escape from the solvent cage even in rigid media. Otherwise, a recombination may be expected.

The transformation of the square pyramidal M(CO)₅ or, better, [M(CO)₅(solvent)] to the trigonal bipyramidal isomer at the softening point of alkane glasses was rejected recently.[27,28] Although proof is still missing, it was suggested that in fluid solutions polynuclear complexes are formed.[28] Thus (OC)₅W(CO)W(CO)₅ was proposed to be the long-lived intermediate in the photolysis of W(CO)₆ in inert solvents at room temperature, thereby accounting for the slow regeneration of W(CO)₆ even in the presence of an excess of CO.[21] A weakly interacting solvent molecule as ligand in M(CO)₅L should be replaced easily by CO. The binuclear complex could be formed by the reaction of W(CO)₅ with W(CO)₆, which may coordinate via oxygen of one of its CO ligands to the W(CO)₅ fragment.

In addition to the low-temperature photolysis of M(CO)₆ in rigid media, attempts have been made to characterize the primary photoproduct of

M(CO)$_6$ by flash photolysis. Nasielski and co-workers observed two transients.[31] The first one ($\lambda_{max} = 483$ nm) did not react with CO. It was converted with a half-life of 6 msec to the second transient ($\lambda_{max} = 445$ nm), which decayed only slowly by second-order kinetics. Added CO accelerated the disappearance of the second transient and the regeneration of Cr(CO)$_6$. These intermediates were assumed to be the $C_{4v}$ and $D_{3h}$ isomers of Cr(CO)$_5$ since their absorption spectra were similar to those obtained in the early study of the photolysis of Cr(CO)$_6$ in low-temperature glasses of hydrocarbons.[24] However, the existence of a $D_{3h}$ isomer of Cr(CO)$_5$ is doubtful (see p. 000). In addition, it is hard to explain why this isomer, but not the $C_{4v}$ form, should react with CO to regenerate Cr(CO)$_6$. Finally, the suggestion that the second transient may be a binuclear chromium carbonyl,[21,27] which must be formed in a bimolecular reaction, is not consistent with the kinetic data which indicate a unimolecular conversion of the first to the second transient.

The results of a very recent flash-photolysis study of Cr(CO)$_6$, which were obtained with a higher time resolution, indicated that neither transient is the proposed $C_{4v}$ or $D_{3h}$ isomer of Cr(CO)$_5$; instead, they are products formed by the reaction of another very short-lived intermediate with impurities of the solvent.[32] The photolysis of Cr(CO)$_6$ in cyclohexane produced the initial transient with a lifetime $>200\ \mu$sec. This transient reacts either with CO or with impurities of the solvent. Although this newly detected intermediate is assumed to be the true Cr(CO)$_5$ species produced in the primary step of the photolysis of Cr(CO)$_6$ in solution, its real identity is also not known since its absorption maximum at 503 nm does not correspond to those obtained by low-temperature photolysis of Cr(CO)$_6$ in alkane glasses or rare-gas matrices.

## III. SUBSTITUTED HEXACARBONYLS OF CHROMIUM, MOLYBDENUM, AND TUNGSTEN

### A. Absorption Spectra

The longest wavelength absorption of monosubstituted hexacarbonyls M(CO)$_5$L is shifted to lower energies compared to M(CO)$_6$.[33-36] Whereas this red shift is small if L is a phosphine or another ligand with good $\pi$-accepting properties, the long-wavelength absorption appears at much lower energies if L is a simple $\sigma$-donating ligand as an amine, ether, or ketone ($\sim$425 nm for Cr(CO)$_5$L [33]). A further substantial shift to lower energy was observed for the first absorption band of the M(CO)$_5$ fragment obtained as photoproduct of M(CO)$_6$ in rare-gas matrices[21,27,29]; this fragment may be regarded as M(CO)$_5$L, where L is a rare-gas atom with

negligible interaction with the metal. The longest wavelength maximum of $Cr(CO)_5$ was found at 542 nm, but was later corrected to be at 623 nm.[33]

These long-wavelength absorptions of $M(CO)_5L$ have been assigned either to $d-d$[33,36-38] or to $d-\pi*(CO)$ CT transitions.[35,35] Although the fairly high intensity of these bands ($\varepsilon > 1000 \ M^{-1} \ cm^{-1}$) may favor a CT assignment, the wavelength dependence on the nature of L is much better explained by a $d-d$ assignment. The degeneracy of the $t_{2g}$ and $e_g$ orbitals of $M(CO)_6$ is removed in $M(CO)_5L$ of $C_{4v}$ symmetry. The $t_{2g}$ states are split into $e$ ($d_{xz,yz}$) and $b_2$ ($d_{xy}$), while the $e_g$ states give $a_1$ ($d_{z^2}$) and $b_1$ ($d_{x^2-y^2}$).

The observation that all $W(CO)_5L$ complexes exhibit their first absorption band at nearly the same wavelength, if L is a $\sigma$-donating ligand, was taken as evidence that the axial ligand field is weak and dominated by the CO trans to L.[36-38] The ordering, $b_2$, $e$, $a_1$, $b_1$, means that the longest wavelength absorption should belong to the lowest energy transition $(e^4b_2^2) \rightarrow (e^3b_2^2a_1)$. The assumption of a weak axial ligand field dominated by the CO *trans* to L requires that the $W(CO)_5$ fragment of $C_{4v}$ symmetry and other $W(CO)_5L$ complexes (L = $\sigma$-donating ligand) all show their long-wavelength absorption at the same energy. While this absorption is only moderately shifted for $W(CO)_5$ (440 nm)[21] compared to $W(CO)_5L$ ($\sim$400 nm)[36] the shift is much more pronounced for the analogous chromium complexes (see p. 000).

There is no obvious reason why the electronic structures of $Cr(CO)_5L$ should be completely different from those of analogous $W(CO)_5L$. Therefore, another model has been proposed that seems to be in better agreement with the experimental data.[33] The interaction of the four equatorial CO ligands with the metal is assumed to remain essentially unaffected by the axial ligand, L. It follows that the $b_2(d_{xy})$ and $b_1(d_{x^2-y^2})$ orbitals should have the same energies as the $t_{2g}$ and $e_g$ orbitals of $M(CO)_6$. The $e(d_{xz,yz})$ orbitals are lifted above the $b_2$ orbital according to the poorer $\pi$-accepting property of L. The $a_1(d_{z^2})$ orbital is lowered below the $b_1$ orbital if L is a rare-gas atom not interacting with the $a_1$ orbital, or is raised above the $b_1$ orbital if L is a good $\sigma$-donating ligand such as an amine.

This interpretation is consistent with the position of the longest-wavelength absorption being dependent on the nature of L. This band corresponds to the $e \rightarrow b_1$ transition, which is shifted to lower energies with decreasing $\pi$-accepting capacity of L and reaches a nearly constant value for pure $\sigma$-donating ligands. The long-wavelength band is shifted further to the red and assigned to the $e \rightarrow a_1$ transition if L is a rare-gas atom. However, it must be emphasized again that a distinction between LF and CT transitions may become meaningless if the metal orbitals

involved in these transitions are extensively mixed with ligand orbitals as indicated by the high extinction coefficients of the corresponding absorption bands.

Complexes of the type, $M(CO)_4L_2$, where $L_2$ denotes a bidentate aromatic diamine such as 2,2'-bipyridyl (bipy) or 1,10-phenanthroline (phen), exhibit a very broad and intense long-wavelength absorption near 450 nm. The very low energy of the $\pi^*$ states of $L_2$ justifies the $d-\pi^*(L_2)$ CT assignment of this band.[39,40] The impressive solvochromic behavior of these complexes with solvent-dependent shifts of the long-wavelength band up to 4000 cm$^{-1}$ gives additional support for the CT assignment.[40,41]

## B.  Emission Spectra

Metal carbonyls and their derivatives generally do not exhibit any luminescence. Recently, however, some substituted hexacarbonyls have been shown to luminesce at low temperatures. The red emission of $M(CO)_4$ (bipy) (M = Cr, Mo, W) was attributed to the spin-forbidden triplet singlet CT transition from the $\pi^*$ state of bipy to the $d\pi$ orbitals of the metal.[42] Also, some monosubstituted tungsten carbonyls, $W(CO)_5L$, where L is a simple $\sigma$ donor (amines, ethers, ketones), luminesce at approximately 530 nm in glasses of methylcyclohexane at 77°K.[36,37] Even $W(CO)_5$ produced by the photolysis of $W(CO)_6$ in methylcyclohexane glasses was found to emit, again at 533 nm. However, the identity of this latter emitting species is not yet clear. First, "true" noninteracting $W(CO)_5$ would be expected to emit at longer wavelength than the other $W(CO)_5L$ complexes because of the shift of the first absorption maximum (see above). Second, $W(CO)_5$ was found to emit only if the CO released in the photolysis of $W(CO)_6$ was removed. To do this the low-temperature glass was probably melted, but it is not yet known to what species $W(CO)_5$ is converted in fluid solution.[21,28] It was shown recently that impurities (possibly ketones), which are always present in very small concentrations in hydrocarbon solvents, can effectively quench $M(CO)_5$.[32] It is possible, therefore, that some $W(CO)_5L$ species caused the emission that was attributed to $W(CO)_5$. The emission of the $W(CO)_5L$ complexes was assumed to be associated with the lowest triplet-to-singlet LF transition, $a_1 \rightarrow e$. However, since the lowest LF transition may be actually $b_1 \rightarrow e$,[33] the emission could belong to the corresponding spin-forbidden transition. It was suggested that at low temperatures all excited species decay by way of the lowest triplet irrespective of excitation wavelength.[37] The observed variation of relative quantum yields and lifetimes of emission of the various $W(CO)_5L$ complexes was attributed to the influence of L on the rate of radiationless deactivation processes. In solution at room temperature no luminescence was observed. It was suggested that this

quenching is associated with fast photochemical reactions that success-fully compete with emission. The emitting triplet state was observed not only in emission but also in absorption as a weak shoulder at the long-wavelength tail of the lowest spin-allowed band. This spin-forbidden transition of the corresponding chromium and molybdenum complexes was seen neither in absorption nor in emission. Both effects are probably associated with the smaller spin-orbit coupling of the lighter metals. The absence of emission may be due to the lack of efficient intersystem crossing from higher excited states to the emitting triplet. As another reasonable explanation, one can assume that the triplet is populated by intersystem crossing from higher excited states (this is a quite common behavior even if the population from the ground state is strongly forbidden[43]), but its radiative deactivation may be too slow to compete with other nonradiation processes.

### C.   Photochemical Reactions

Excited LF states of $M(CO)_5L$ may lead to a destabilization of M—Co and M—L bonds. The transition, $d_{xz,yz} \rightarrow d_{x^2-y^2}$, is expected to labilize preferentially equatorial M—CO bonds if L is a $\sigma$-donating ligand that does not interact with the orbitals involved in this transition. With growing $\pi$-accepting capacity of L, the $d_{xz,yz}$ orbitals become increasingly bonding. Hence $d_{xz,yz}$ to $d_{x^2-y^2}$ transitions may also destabilize axial M—CO and M—L bonds. Also, these bonds should be weakened by $d_{xz,yz}$ to $d_{z^2}$ transitions. CT transitions from the metal to $\pi^*(CO)$ states, which should occur at higher energies, could also lead to a labilization of M—CO and M—L bonds if the $\pi^*(CO)$ states are extensively mixed with metal orbitals. Even a CT transition from a $d$ to a noninteracting $\pi^*(CO)$ orbital may initiate a substitution reaction by facilitating a nucleophilic attack of a substituting ligand at the metal.

Both photochemical reactions of $M(CO)_5L$, that is, substitution of L and of CO, are observed. However, the mechanism of these photoreac-tions and the interdependence of L versus CO substitution is not at all clear. Strohmeier postulated that $M(CO)_5L$ photodissociates into $M(CO)_4L$ and $M(CO)_5$ simultaneously with an overall quantum yield of one.[6,44,45] This assumption was based on two observations. Upon irradia-tion of $M(CO)_5$(pyridine) in the presence of an excess of pyridine, $M(CO)_4$(pyridine)$_2$ was produced with quantum yields between 0.05 and 0.3. While the first intermediate, $M(CO)_4$(pyridine), yields the product, $[M(CO)_4(pyridine)_2]$, the second intermediate, $M(CO)_5$, should react with additional pyridine to give back the starting complex, which does not contribute to the net reaction. If $Cr(CO)_5$(pyridine) was irradiated in the presence of added CO, $Cr(CO)_6$ was regenerated. This observation was

taken as evidence for the formation of the second intermediate, $Cr(CO)_5$. The quantum yield of the production of $M(CO)_4(pyridine)_2$ was found to be solvent dependent, and it was considerably lower for excitation at 436 nm than at 366 nm. The postulation that both intermediates are formed with an overall quantum yield of unity leads to the conclusion that the formation of $M(CO)_5$ should be favored at longer wavelengths. This assumption implicates the participation of two different excited states as precursors for both reaction modes.

Basically the same conclusions were drawn from a recent study by Wrighton, Hammond, and Gray.[38] $W(CO)_5(pyridine)$ dissolved in isooctane was found to give $cis$-$[W(CO)_4(pyridine)_2]$ upon irradiation in the presence of added pyridine. The quantum yield increased with decreasing wavelength of irradiation, from $\phi = 0$ at 436 to $\phi = 0.3$ at 254 nm. In the presence of 1-pentene instead of pyridine, $W(CO)_5(pentene)$ was produced; the quantum yields increased with increasing irradiating wavelength from $\phi = 0.3$ at 254 nm to $\phi = 0.63$ at 436 nm. The substitution of coordinated pyridine by pentene was explained by the assumption that the irradiation (436 nm) of the longest-wavelength band of $W(CO)_5(pyridine)$ is associated with the lowest energy transition ($d_{xz,yz}$ to $d_{z^2}$) that should labilize the ligands on the $z$ axis. However, it should not be the pyridine but the axial CO ligand that is expected to be dissociated since the axial ligand field was assumed to be dominated by the CO $trans$ to pyridine.[36,37] Shorter-wavelength irradiation was suggested to lead to the population of the next higher excited state ($d_{xz,yz}$ to $d_{x^2-y^2}$), which initiates the release of an equatorial CO ligand, yielding $cis$-$[W(CO)_4(pyridine)_2]$ in the presence of an excess of pyridine. But the internal conversion to the lowest excited state ($d_{xz,yz}$ to $d_{z^2}$) must be very fast to explain the small quantum yield of CO and the large efficiency of pyridine substitution upon shorter-wavelength irradiation. However, some critical remarks concerning these results still must be made.

The quantum yields of the formation of $W(CO)_4(pyridine)_2$ in isooctane reported by Wrighton, Hammond, and Gray[38] are much lower than those found by Strohmeier and von Hobe[45] for the same reaction in THF or benzene. Since the concentrations of pyridine used in the latter experiments were four times as high as those in the former ones, there is some evidence that the quantum yield is not only solvent dependent but varies also with the concentration of the substituting ligand. The concentration of pentene used for determinations of the quantum yield of formation of $W(CO)_5(pentene)$ was more than fifteen times as high as that of pyridine in the reaction with $[W(CO)_5(pyridine)]$.[38] Hence the significance of these data seems to be doubtful. No explanation was given for the absence of any $[W(CO)_4(pyridine)(pentene)]$, which, according to the mechanism

suggested above, should have been formed in addition to [W(CO)$_5$(pentene)] upon shorter-wavelength irradiation of [W(CO)$_5$(pyridine)] in the presence of pentene. The assumption that the production of *cis*-[W(CO)$_4$(pyridine)$_2$] is directly related to the photodissociation of an equatorial CO ligand of [W(CO)$_5$(pyridine)] seems to be supported by the observation that the photoexchange of [M(CO)$_5$(piperidine)] (M = Mo, W) with labeled CO takes place preferentially at an equatorial coordination position.[46] In the case of M(CO)$_5$[P(C$_6$H$_5$)$_3$] (M = Mo, W), an axial CO was exchanged. It is possible that this difference is associated with the σ-donor character of piperidine and the π-acceptor strength of P(C$_6$H$_5$)$_3$. However, no such relationship is apparent if the substituting ligand is a phosphine or an amine instead of CO.

Other properties, such as steric ones, may be responsible for the stereospecific photoproduction of disubstituted hexacarbonyls. In contrast to the observation that W(CO)$_5$(pyridine) undergoes a photosubstitution of pyridine with high quantum yields, the study by Darensbourg et al.[46] led to the conclusion that the light sensitivity of M(CO)$_5$L complexes, including W(CO)$_5$L, is restricted to M—CO bonds, while the M—L bonds are photochemically very stable. Much of this confusion can be avoided by simultaneous quantum-yield determinations for the conversion of M(CO)$_5$L to M(CO)$_4$LL' and M(CO)$_5$L' under variation of the solvent and determining the nature and the concentration of the substituting ligand. It is clear that L must be different from L' to obtain unambiguous results.

An interpretation of the photochemistry of M(CO)$_5$L complexes can not yet be given because of the various conflicting observations. However, there is also some indication that the photochemical substitution may not proceed by a dissociative release of coordinated ligands but, instead, by an associative reaction of the substituting ligand with the complex in its excited state. A heptacoordinated intermediate may rearrange to yield M(CO)$_4$LL' or M(CO)$_5$L'. In contrast to the pure hexacarbonyls, their monosubstituted derivatives have not been observed to undergo any photodissociation in inert solvents. In addition, while M(CO)$_5$L complexes were clearly demonstrated to undergo a photosubstitution of CO in the presence of strong σ-donating or π-accepting ligands, L', to yield M(CO)$_4$LL'[46] (L = L'),[6,7] CO substitution is apparently not achieved in the presence of weak nucleophiles such as pentene.[38] A dissociative reaction should not depend that much on the nature of the substituting ligand. Additional support for an associative mechanism comes from the variation of the quantum yield with the solvent and, probably, the concentration of the substituting ligand.

Upon irradiation of the long-wavelength absorption of the M(CO)$_5$ fragment produced by the photolysis of M(CO)$_6$ in low-temperature

glasses of inert hydrocarbons or rare-gas matrices, the regeneration of M(CO)$_6$ was observed.[21,29,36] Since M(CO)$_5$ may be regarded as a monosubstituted hexacarbonyl with a noninteracting ligand in the sixth coordination position, the observed photoreversal can be considered as photosubstitution of a M(CO)$_5$L complex that takes place even at low temperatures. However, this photoreversal seems to be a quite general behavior of metal carbonyls photolyzed in low-temperature media and independent of the geometry and electronic structure of the metal carbonyl fragment.[47,48] Therefore, it was suggested that the photoregeneration of M(CO)$_6$ does not involve excited-state chemistry.[21,28] According to this assumption, the photoreversal is facilitated by a local softening of the low-temperature medium that occurs on conversion of the absorbed light to heat by radiationless deactivation of excited M(CO)$_5$ to its ground state. The CO molecule, which is assumed to be ejected from the matrix cage when M(CO)$_6$ is photolyzed, may then recombine with the M(CO)$_5$ fragment by diffusion, as it does at higher temperatures without irradiation.

The photosubstitution of hexacarbonyls does not end when two CO ligands are replaced. Under favorable conditions, continued irradiation of dissolved hexacarbonyls leads to the substitution of five or even all six CO groups if a replacing ligand, such as P(OCH$_3$)$_3$ or P(OCH$_3$)$_2$F, has good $\pi$-acceptor properties and can stabilize the zerovalent metal.[49]

The arene M(CO)$_3$ complexes constitute a category of substituted hexacarbonyls deserving special attention. These compounds may be regarded as pseudooctahedral complexes where three ligand positions are occupied by an arene ring. The metal-arene bonding is achieved by the interaction of the $\pi$ orbitals of the aromatic ring with metal orbitals. The absorption spectrum of C$_6$H$_6$Cr(CO)$_3$ shows an intense long wavelength band at 320 nm with a shoulder at 376 nm. These bands were assigned to a CT transition from Cr to the benzene ring and, to a lesser extent, to the carbonyl groups.[50] The next band at 260 nm was assigned to a CT transition from Cr to the carbonyls. Upon irradiation of solutions of C$_6$H$_6$Cr(CO)$_3$ at 366 nm into the long-wavelength absorption of the complex, coordinated CO was exchanged with labeled CO,[51] or replaced by another ligand present in the solution.[6,7] In addition, a photoexchange of coordinated benzene with labeled benzene was observed.[52] It becomes increasingly difficult to achieve a photoexchange of CO or arene for the corresponding complexes of the heavier metals, Mo and W. However, the relative rate of exchange of toluene in CH$_3$C$_6$H$_5$W(CO)$_3$ was increased by shorter-wavelength irradiation at 254 nm. These results indicate either a hot-molecule mechanism or the participation of higher excited states in

the photoexchange of coordinated arenes. The intermediate formation of a $M(CO)_3$ fragment was postulated to occur in this photoreaction. But it seems more likely that the photoexchange of arenes takes place by a bimolecular reaction.

## IV. CARBONYLS OF MANGANESE AND RHENIUM

Diamagnetic $Mn_2(CO)_{10}$ is composed of two square pyramidal $Mn(CO)_5$ units linked by a metal-metal bond. The whole molecule is staggered and, therefore, of $D_{4d}$ symmetry. The highest occupied orbitals are the six $d_{xz}$, $d_{yz}$, $d_{xy}$ $\pi$ orbitals ($e_1$, $e_2$, $e_3$), and the $d\sigma$ (M—M) orbital ($a_1$), which is the bonding combination of the $d_{z^2}$ orbitals of both manganese atoms and represents the metal-metal bond of $Mn_2(CO)_{10}$. Photoelectron spectroscopy provides evidence that the $d\sigma$(M—M) lies slightly above the $d\pi$ orbitals.[53] Since the lowest empty MO is anticipated to be the antibonding $d\sigma^*$(M—M) orbital ($b_2$), the intense long-wavelength band in the absorption spectrum of $Mn_2(CO)_{10}$ at 340 nm ($\varepsilon \sim 2 \times 10^4\,M^{-1}\,cm^{-1}$), which is polarized along the metal-metal axis, is assigned to the allowed transition from $d\sigma$(M—M) to $d\sigma^*$(M—M).[54] Due to the small energy difference between $d\sigma$(M—M) and $d\pi$ orbitals, $d\pi \rightarrow d\sigma^*$(M—M) transitions may contribute to the intensity of this first absorption. A shoulder on the long-wavelength tail of this band has been assigned to a $d\pi \rightarrow d\sigma^*$(M—M) transition, but such an assignment would require that the $d\pi$ levels lie above the $d\sigma$(M—M) orbital. The intense near-ultraviolet absorption of $Re_2(CO)_{10}$ at 310 nm ($\varepsilon \sim 17,000$) is also assigned to the $d\sigma$(M—M) $\rightarrow d\sigma^*$(M—M) transition.

The formation of $Mn(CO)_5$ or $Re(CO)_5$ radicals, or at least a destabilization of the metal-metal bond, may be expected if the irradiation of $Mn_2(CO)_{10}$ or $Re_2(CO)_{10}$ is associated with the $d\sigma$(M—M) $\rightarrow d\sigma^*$(M—M) transition. In addition, a labilization of M—CO bonds is possible if the irradiation leads to some extent to the excitation of a $\pi$-bonding $d$ electron in the $d\pi \rightarrow d\sigma^*$(M—M) transition.

Although no photochemical reaction of $Mn_2(CO)_{10}$ was observed in inert solvents, evidence for the formation of manganesecarbonyl radicals was obtained if $Mn_2(CO)_{10}$ was photolyzed with long-wavelength irradiation ($\lambda = 436$ nm) in halogen-containing solvents.[55–57] The photolysis of $Mn_2(CO)_{10}$ in the presence of HBr in cyclohexane led to the almost quantitative formation of $Mn(CO)_5Br$.[58] Irradiation of $Mn_2(CO)_{10}$ in the halocarbon solvent, $CCl_4$, produced $Mn(CO)_5Cl$ and $CCl_3$ radicals, which are used to initiate polymerization reactions.

It may be expected that the primary step in these photolyses is the

homolytic cleavage into two $Mn(CO)_5$ radicals initiated by the $d\sigma(M—M) \rightarrow d\sigma^*(M—M)$ transition. An alternative possibility for the halogen abstraction is the interaction of the halogen-containing compound with $Mn_2(CO)_{10}$ in its $d\sigma \rightarrow d\sigma^*$ excited state.[59] However, the analysis of the kinetic data and the quantum-yield determinations of this photoreaction led to the conclusion that the photoprimary step is an unsymmetric cleavage of the metal-metal bond producing $Mn(CO)_4$ and $Mn(CO)_6$ radicals.[55-57] Their subsequent reactions are complicated processes. In contrast to these results, evidence was obtained recently that the photolysis of $Re_2(CO)_{10}$ in $CCl_4$ at 313 or 366 nm, corresponding to the $d\sigma \rightarrow d\sigma^*$ transition, leads to a symmetric metal-metal bond cleavage in the photoprimary step.[60] With 313-nm radiation $Re_2(CO)_{10}$ disappeared with a quantum yield of 0.6, while $Re(CO)_5Cl$, which is assumed to be formed by the reaction of $Re(CO)_5$ with $CCl_4$, was produced with a quantum yield of 1.2. Other observations also support a light-induced homolytic cleavage of M—M bonds. Upon irradiation of a mixture of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ in hexane some $MnRe(CO)_{10}$ was formed.[61] The photolysis of $(OC)_5Mn—Mn(CO)_3L_2$ ($L_2$ = phen or bipy) in ether or benzene yielded $Mn_2(CO)_{10}$ and $[Mn(CO)_3L_2]_2$.[62,63] The irradiation of $(OC)_5Mn—Re(CO)_3(phen)$ in THF produced $Mn_2(CO)_{10}$ and $[Re(CO)_3(phen)]_2$.[64]

A CTTS excited state in $CCl_4$, which initiates the photochemical oxidation of ferrocene in $CCl_4$,[7] can be excluded as precursor for the photooxidation of $Mn_2(CO)_{10}$ or $Re_2(CO)_{10}$ to $Mn(CO)_5Cl$ or $Re(CO)_5Cl$ because the absorption spectra of $M_2(CO)_{10}$ dissolved in inert solvents such as benzene does not show a new CT-to-solvent band on addition of $CCl_4$.[56]

Although $Mn_2(CO)_{10}$ does not undergo any photochemical reaction in inert solvents, a photosubstitution of coordinated CO does take place in the presence of potential ligands. This behavior may reflect the contribution of $d\pi–d\sigma^*(M—M)$ transitions to the long-wavelength absorption of $Mn_2(CO)_{10}$. Up to three CO groups may be replaced, depending on the substituting ligand. In the presence of simple nitrogen bases only one equatorial CO was substituted.[65] Ligands with good $\pi$-acceptor properties (phosphines, arsines) can replace one[65] or two[66] axial CO groups. $PF_3$ can photosubstitute up to three CO ligands in axial and equatorial positions, while the thermal reaction led only to the substitution of axial CO ligands.[67] It is also feasible that the photosubstitutions do not take place at the intact $Mn_2(CO)_{10}$ molecule.[67] If manganesecarbonyl radicals, $Mn(CO)_5$, are formed in the photoprimary step, these radicals may undergo a substitution of CO. The recombination of the substituted radicals should then yield the most stable isomer. A similar mechanism was also suggested for thermal reactions of manganese carbonyls.[68,69]

## V. SUBSTITUTED MANGANESECARBONYLS

The manganese atom in the pseudooctahedral complexes, $Mn(CO)_5X$ ($X = Cl$, $Br$, $I$), can be regarded as a formally unipositive ion with six $d$ electrons. Photoelectron spectroscopy shows that the highest filled orbitals of these complexes are $\pi$ orbitals of primarily halogen character.[53,70] Slightly below these orbitals are the $p\sigma(X)$ and $d\pi$ orbitals of manganese. The lowest empty antibonding states are expected to be $d\sigma$ below $\pi^*(CO)$ orbitals.[71] From this ordering, low-energy X-to-Mn, X-to-CO, and Mn-to-CO CT transitions and LF transitions can be anticipated. The longest-wavelength band in the absorption spectrum of $Mn(CO)_5X$ was assigned to a $\pi(X)–\pi^*(CO)$ CT transition.[71] Other low-energy bands were assumed to be less intense and hidden under the X-to-CO CT band, which showed a solvent-dependent shift. This shift was attributed to the interaction of the $\pi$ electrons of the halogen with the solvent.

Although no detailed investigation of the photochemistry of the manganese carbonyl halides complexes has yet been published, it was shown that irradiation of dissolved $Mn(CO)_5X$ may lead to the release of CO.[72] $Mn(CO)_5Br$ was observed to undergo a photoexchange with labeled CO.[73] In contrast to the thermal exchange, the photoexchange did not proceed stereospecifically. The thermal dimerization of $Mn(CO)_5Br$ to $[Mn(CO)_4Br]_2$, which occurs with release of CO and the formation of two Br bridges linking the metal centers, was shown to take place faster if the long-wavelength band of $Mn(CO)_5Br$ was irradiated.[72] Also, the irradiation of $Re(CO)_5Cl$ produced $[Re(CO)_4Cl]_2$.[60] Interestingly, $[Mn(CO)_4Br]_2$ underwent a photoredox reaction according to the equation[72]

$$2[Mn(CO)_4Br]_2 \rightarrow Mn_2(CO)_{10} + 2MnBr_2 + 6CO \qquad (6\text{-}1)$$
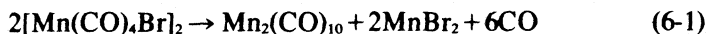
At present, no explanation for this photoredox behavior can be given. The long-wavelength band that was irradiated in the photolysis of $[Mn(CO)_4Br]_2$ was assigned to a $d\pi–\pi^*(CO)$ CT transition.[71]

The ligand, X, in the complexes, $Mn(CO)_5X$ ($X = H$, $CH_3$, $CF_3$), does not have any $\pi$-bonding properties. From photoelectron spectroscopy,[53] the highest filled orbitals were assigned to be either $d\pi$-bonding[53,74] or $\sigma$-bonding orbitals of X.[75] The $d\pi$ and $\sigma(X)$ levels are certainly close in energy. The lowest empty antibonding orbitals are again assumed to be $d\sigma$ below $\pi^*(CO)$ states.[71] The excitation of a bonding $\sigma(X)$ electron may lead to a homolytic splitting of the Mn—X bond, whereas $d\pi–d\sigma$ or $d\pi–\pi^*(CO)$ transitions could lead to a labilization of Mn—CO bonds. The long-wavelength band in the absorption spectra of $Mn(CO)_5X$ was assigned to a $d\pi–\pi^*(CO)$ transition.[71] This band may obscure other bands of lower intensity.

The photolysis of $HMn(CO)_5$ does not seem to lead to a homolytic splitting of the H—Mn bond. The loss of an equatorial CO group with formation of trigonal bipyramidal $HMn(CO)_4$ was observed when $HMn(CO)_5$ was irradiated at 229 nm in an argon matrix at 15°K.[47] A regeneration of $HMn(CO)_5$ occurred for long-wavelength irradiation at $\lambda > 285$ nm. The photolysis of $HMn(CO)_5$ in the presence of $PF_3$ led to the substitution of CO by $PF_3$.[76] In contrast to the photochemical stability of the H—Mn bond of $HMn(CO)_5$, the irradiation of $HMn(CO)_3(PR_3)_2$ in $CCl_4$ produced $ClMn(CO)_3(PR_3)_2$ and, most likely, $CHCl_3$.[77] In analogy to the photolysis of $Re_2(CO)_{10}$ in $CCl_4$,[60] the irradiation of $HMn(CO)_3(PR_3)_2$ may lead to an excitation of a H—Mn $\sigma$-bonding electron and the subsequent homolysis of the H—Mn bond. The radicals, H and $Mn(CO)_3(PR_3)_2$, may then react with $CCl_4$ to yield $ClMn(CO)_3(PR_3)_2$ and $CHCl_3$.

When $CH_3Mn(CO)_5$ was irradiated (230 nm $< \lambda <$ 280 nm) in an argon matrix at 15°K, the loss of one CO ligand was observed.[78,79] This photolysis may be reversed with long-wavelength irradiation at $\lambda >$ 280 nm.[79] The release of CO was also shown to occur if $CF_3Mn(CO)_5$ was photolyzed under similar conditions.[78] In the presence of $PF_3$ at room temperature the photolysis of $HC_2F_4Mn(CO)_5$ led to a substitution of CO by $PF_3$.[76] Although the low-temperature photolysis of $CR_3Mn(CO)_5$ complexes provides definite evidence only for the release of CO, other observations suggest that the irradiation of $CH_3Mn(CO)_5$ may also lead to the cleavage of the $CH_3$—Mn bond, possibly caused by the excitation of a $\sigma$-bonding electron. The photolysis of $CH_3Mn(CO)_5$ in the presence of $CClF=CF_2$ led to an insertion of the olefin into the carbon-manganese bond with formation of $CH_3CF_2CFClMn(CO)_5$.[80] The photochemical insertion was also achieved with hexafluoro-1,3-butadiene.[81]

$C_5H_5Mn(CO)_3$ may be regarded as a pseudooctahedral complex. The uninegative aromatic cyclopentadienyl ring occupies three ligand positions. The central manganese is formally unipositive with six $d$ electrons. The electronic spectrum of $C_5H_5Mn(CO)_3$ is known,[82] but no band assignments have been made. A characteristic feature of the photochemistry of $C_5H_5Mn(CO)_3$ is its striking similarity to that of the hexacarbonyls, $M(CO)_6$. Upon irradiation in organic solvents, $C_5H_5Mn(CO)_3$ releases one CO ligand with a quantum yield of unity that is independent of the irradiation wavelength.[45] The formation of a $C_5H_5Mn(CO)_2$ fragment was observed upon irradiation of $C_5H_5Mn(CO)_3$ in glasses of inert hydrocarbons at low temperatures.[83] Softening of the glass at higher temperatures led to a regeneration of $C_5H_5Mn(CO)_3$. The photolysis of $C_5H_5Mn(CO)_3$ in the presence of potential ligands was used to synthesize numerous complexes of the general formula, $C_5H_5Mn(CO)_2L$.[6,7] Further

photolysis may lead to the substitution of the second or even the third CO ligand. For example, $C_5H_5Mn(PF_3)_3$ was prepared by the irradiation of $C_5H_5Mn(CO)_3$ in THF solution in the presence of $PF_3$.[84]

$Mn(CO)_4NO$ is isoelectronic and isostructural with $Fe(CO)_5$. However, the ordering of the electronic energy levels of $Mn(CO)_4NO$ is not known and may be quite different from that of $Fe(CO)_5$ because of the influence of the NO group. Nevertheless, the main features of the photochemistries of the two complexes seem to be quite similar. The irradiation of $Mn(CO)_4NO$ in low-temperature glasses leads to the release of one CO ligand and the formation of a $Mn(CO)_3NO$ fragment.[85] If the photolysis of $Mn(CO)_4NO$ is carried out at room temperature, this fragment apparently adds to an intact $Mn(CO)_4NO$ molecule to yield $Mn_2(CO)_7(NO)_2$.[86]

Photochemical substitution reactions of $Mn(CO)_4NO$ were investigated in a detailed study by Keeton and Basolo.[87] Upon irradiation of dissolved $Mn(CO)_4NO$ in the presence of a substituting ligand, L, $[Mn(CO)_3(NO)L]$ was produced with a quantum yield that was dependent upon the nature and the concentration of the nucleophile, L. If L was the relatively weak nucleophile, $As(C_6H_5)_3$, the quantum yield at 427-nm irradiating wavelength was 0.15 and independent of the concentration of $As(C_6H_5)_3$. In the case of the stronger nucleophile, $P(C_6H_5)_3$, the quantum yield increased with increasing concentration of $P(C_6H_5)_3$. The quantum yield at low concentrations of $P(C_6H_5)_3$ was found to have a lower limit. This limiting value was nearly equal to the concentration-independent quantum yield for the formation of $Mn(CO)_3(NO)As(C_6H_5)_3$.

Since two absorption bands in the spectrum of $Mn(CO)_4NO$ are overlapping at the irradiating wavelength, it was suggested that two different excited states may be involved in the photochemical substitution. The higher-energy band, which was estimated to account for 20% of the absorption at the irradiating wavelength, was assumed to belong to a LF transition. This LF excited state should then lead to a spontaneous release of CO and formation of a $Mn(CO)_3NO$ intermediate, which reacts with the nucleophile according to a SN1 mechanism. The quantum yield is then expected to be independent of the concentration and nucleophilicity of the substituting ligand. The second excited state, which was assumed to be associated with the lower-energy band, was tentatively assigned to a metal-to-NO CT transition. The CT excited complex should be accessible to the attack of a strong nucleophile such as $P(C_6H_5)_3$. Some evidence was obtained for the intermediate formation of $[Mn(CO)_4(NO)][P(C_6H_5)_3]$, which finally releases CO to yield $[Mn(CO)_3(NO)][P(C_6H_5)_3]$. This SN2 path for the formation of the photoproduct would explain the concentration-dependent quantum yield at higher $P(C_6H_5)_3$ concentrations. The possible formation of $Mn_2(CO)_7(NO)_2$ as an intermediate (see

above) that may interfere with the discussed mechanism was not examined.

## VI. IRONPENTACARBONYL

$Fe(CO)_5$ has a trigonal bipyramidal structure. The formally zerovalent iron atom has a $d^8$ electron configuration. Semiempirical calculations have shown that the highest filled MOs are derived from the metal $d_{x^2-y^2}$ and $d_{xy}$ orbitals which interact with $\sigma$ orbitals of suitable CO ligands.[88] Since $\pi$ interaction is negligible, the resultant two MOs ($e'$ in $D_{3h}$), which contain about 30% of ligand $\sigma$-orbital character, are slightly antibonding. The next lower filled orbitals ($e''$) are derived from $d_{xz}$ and $d_{yz}$ metal orbitals. Since these two metal orbitals interact only with $\pi(CO)$ orbitals, the resultant MOs should be bonding. This ordering of the highest filled orbitals of $Fe(CO)_5$ was confirmed by photoelectron spectroscopy.[13] The lowest unfilled MO was assumed to be derived from the $d_{z^2}$ metal orbital.[88] The $d_{z^2}$ orbital of iron interacts strongly with $\sigma$ orbitals of both axial CO ligands to form an antibonding MO ($a_1'$), which, however, has almost 60% ligand character. The next MOs, of mainly $\pi^*(CO)$ character, are placed at higher energies.

The electronic spectrum[88] of $Fe(CO)_5$ exhibits a long-wavelength absorption of moderately high intensity ($\varepsilon = 3800$ M$^{-1}$ cm$^{-1}$) at 35,500 cm$^{-1}$. This band was assigned to lowest-energy transition, $e'(d_{x^2-y^2}, d_{xy}) \rightarrow a_1'(d_{z^2})$, which is spin- and symmetry-allowed. The same transition was also assigned[13] to a weak shoulder at 28,200 cm$^{-1}$, which was observed in an older study,[89] but may be due to impurities of $Fe_2(CO)_9$ (solid $Fe_2(CO)_9$ has an absorption band at 25,300 cm$^{-1}$ [90]). The next absorption bands of higher intensities at shorter wavelength should belong to Fe-to-CO CT transitions.

Upon irradiation, $Fe(CO)_5$ loses one CO ligand in the primary photochemical step. It seems likely that this photoreaction is associated with the lowest energy transition $e'$–$a_1'$.[88] It is probably not the removal of an electron from a nearly nonbonding MO but the addition to the strongly antibonding $d_{z^2}$ orbital that causes the release of a CO ligand that should be an axial one.

The mechanism of the photochemical release of CO by $Fe(CO)_5$ and the nature of the ironcarbonyl fragment, which is formed as an intermediate in the primary photochemical step, have been investigated in several studies. In the absence of substituting ligands, the photolysis of $Fe(CO)_5$ yields $Fe_2(CO)_9$. Labeled CO was incorporated into $Fe_2(CO)_9$ only to a small extent when the gas phase photolysis of $Fe(CO)_5$ was carried out in the presence of $^{14}CO$.[91] It was suggested that electronically excited $Fe(CO)_5$ does not lose CO; instead, it reacts with a ground-state molecule

of $Fe(CO)_5$ to yield $Fe_2(CO)_9$ with loss of CO. Later studies, however, provided compelling evidence that the primary photochemical step of excited $Fe(CO)_5$ is indeed the loss of one CO ligand. The small incorporation of labeled CO into $Fe_2(CO)_9$ may be explained by the assumption that the reaction of the $Fe(CO)_4$ intermediate with $Fe(CO)_5$ is much faster than its reaction with CO.[7] In solutions of inert hydrocarbons the formation of $Fe_2(CO)_9$ was slow enough to demonstrate that an efficient photoexchange between $Fe(CO)_5$ and $C^{18}O$, as well as a photochemical scrambling of coordinated CO between $Fe(CO)_5$ and $Fe(C^{18}O)_5$, takes place.[92] These observations are consistent with the assumption that $Fe(CO)_5$ photodissociates into $Fe(CO)_4$ and CO. The thermal regeneration of $Fe(CO)_5$ then accounts for the exchange of CO.

Additional evidence for the loss of CO in the first step was provided by the results of the photolysis of $Fe(CO)_5$ in low-temperature glasses and matrices. The infrared spectra of irradiated $Fe(CO)_5$ in hydrocarbon glasses at 77°K indicated the formation of a $Fe(CO)_x$ species that could not be identified.[24] On melting the rigid glass, a new infrared band developed at $1834 \, cm^{-1}$, which was probably due to the formation of $Fe_2(CO)_9$.[7] In an argon matrix containing 20% CO no indication for a photochemical change was obtained.[90] The infrared spectra of $Fe(CO)_5$ in a pure argon matrix at 15 or 20°K showed that $Fe(CO)_5$ could be photolyzed only to a small extent.[93] The photoproduct was not identified. However, $C^{18}O$ was photochemically incorporated in $Fe(CO)_5$ when the argon matrix was doped with labeled CO.[90] Apparently, a fast reversal of the photolysis occurred even in rigid media at low temperatures. Only recently, Poliakoff and Turner showed that this regeneration was promoted by the light of the Nernst glower that was used in the analyzing infrared spectrometer.[48] Upon irradiation with a medium-pressure mercury arc, an efficient photolysis of $Fe(CO)_5$ in a neon matrix at 4°K was observed using infrared spectroscopy provided that the ultraviolet and visible light was removed from the infrared spectrometer beam by suitable filters. The analysis of the infrared spectra led to the conclusion that the photoproduct was a $Fe(CO)_4$ species that has a distorted tetrahedral structure. This distortion is probably due to the Jahn–Teller effect, which is expected to occur in tetrahedral $d^8$ complexes. The distortion was not caused by the matrix since similar results were obtained for a variety of matrices at 20°K. A reversal of the photolysis took place by warming the matrix or upon irradiation of the $Fe(CO)_4$ fragment, which has an absorption maximum at 320 nm. The photoreversal was assumed to be a thermal process initiated by the conversion of light to heat. Upon irradiation of $Fe(CO)_5$ in argon matrices doped with ethylene, the formation of $Fe(CO)_4C_2H_4$ was observed.[94]

The detection of a $Fe(CO)_4$ species by flash photolysis of $Fe(CO)_5$ in the gas phase[95] or in solution has not yet been successful.[96] A long-lived transient with a half-life of 0.3 sec that was observed in the flash photolysis of $Fe(CO)_5$ in benzene[97] was probably a complex with benzene weakly coordinated to $Fe(CO)_4$.[98]

Whereas the photolysis of $Fe(CO)_5$ in solution yields $Fe_2(CO)_9$ as final product, complexes of the type, $Fe(CO)_4L$, are formed when the irradiation is carried out in the presence of substituting ligands. Numerous substituted ironcarbonyls with a great variety of ligands have been prepared in this way.[6,7] According to the results presented above, a $Fe(CO)_4$ intermediate reacts with suitable ligands to give $Fe(CO)_4L$.

Another interesting aspect of these photosubstitutions is their stereochemical course since, as already mentioned, absorption of light into the long-wavelength band of $Fe(CO)_5$ should lead to the release of an axial CO ligand. In what may be a contradiction to this prediction the light-induced CO exchange between labeled CO and $Fe(CO)_5$ or $Fe(CO)_4[P(C_6H_5)_3]$ in solutions of hydrocarbons was shown to lead to a statistical distribution of labeled CO in axial and equatorial positions.[92] However, in the presence of other ligands the formation of $Fe(CO)_4L$, induced thermally[99,100,101] or photochemically,[7,102,103] proceeds stereospecifically. Ligands with $\sigma$-donor properties were found to occupy an axial position, while some $\pi$-bonding ligands such as olefins were shown to be coordinated in an equatorial position of the trigonal bipyramidal structure of $Fe(CO)_4L$.[104] Since $Fe(CO)_5$ seems to be stereochemically nonrigid in solution at room temperature,[92,105] it is apparently unclear whether these stereospecific photosubstitutions are dependent on the position of the released CO ligand prior to photolysis. In addition, such a dependence can not be expected if the $Fe(CO)_4$ intermediate adopts a nearly tetrahedral structure, as was suggested by the low-temperature studies.[48] It is probably the most stable isomer formed in the photoreaction. Frequently, a second CO ligand may be photosubstituted also to yield complexes of the formula, $Fe(CO)_3L_2$.[6,7]

With one exception no quantum yields have been reported for photoreactions of $Fe(CO)_5$. As early as 1929, quantum yields for the photochemical decomposition of liquid $Fe(CO)_5$ were obtained.[106] The quantum yield for CO evolution increased from 0.83 at 436 nm to 0.99 at 254-nm irradiating wavelength. Since the photolysis of $Fe(CO)_5$ in the liquid state may be a complicated process, it is difficult to draw conclusions from these results.

Finally, it should be mentioned that an $Fe(CO)_4$ species was also postulated as an intermediate in the photolysis[107] and in the thermal reactions[108] of $Fe_2(CO)_9$. However, the results of a low-temperature study

in inert gas matrices did not give any evidence for the formation of Fe(CO)$_4$. The infrared spectra of photolyzed Fe$_2$(CO)$_9$ indicated the loss of CO under formation of Fe$_2$(CO)$_8$.[90]

## VII.  NICKELTETRACARBONYL

Ni(CO)$_4$ has a tetrahedral structure. The nickel atom has a completely filled $d$ shell and thus contributes ten valence electrons to the bonding of Ni(CO)$_4$. In $T_d$ symmetry the $d$ orbital are split into $t_2$ and $e$ orbitals.[13] The highest filled orbitals of Ni(CO)$_4$ are three degenerate $t_2$ levels that are formed by the antibonding interaction of the $d_{xz}$, $d_{yz}$, and $d_{xy}$ orbitals of nickel with $\sigma$ orbitals of CO. These antibonding $t_2$ levels may also interact weakly with $\pi$(CO) orbitals. In spite of this interaction, the $d$ character should prevail in the $t_2$ states.

The two degenerate $e$ orbitals that are placed below the $t_2$ orbitals are probably nearly pure nonbonding $d_{x^2-y^2}$ and $d_{z^2}$ orbitals that interact only slightly with $\pi$(CO) orbitals. Different calculations have been carried out to determine the energies and populations of the occupied MOs and the charge distribution within Ni(CO)$_4$.[14,17,109] Although the actual values obtained varied with the calculational procedure used, the splitting between the $t_2$ and $e$ orbitals certainly is not large. By photoelectron spectroscopy the energy separation was found to be 0.8 eV ($\sim 6400$ cm$^{-1}$).[13]

Since the $e$ and $t_2$ orbitals are completely filled with ten $d$ electrons provided by the zero-valent nickel, no $d$–$d$ transitions are possible in Ni(CO)$_4$. The lowest empty orbitals are derived from $\pi^*$ states of the CO ligands. Assignments have been made for the absorption bands in the electronic spectrum of Ni(CO)$_4$.[17] Although other assignments could have been obtained using different calculational methods, it seems clear that all absorption bands in the experimentally accessible region of the spectrum belong to $d \rightarrow \pi^*$(CO) CT transitions. For this reason the photochemical behavior of Ni(CO)$_4$ is a valuable test to examine whether it is necessary to invoke LF excited states as precursors for the photodissociation of metal carbonyls. Since Ni(CO)$_4$ is known to release CO upon irradiation, $d \rightarrow \pi^*$(CO) CT excited states are clearly responsible for this photodissociation. Although this result is not proof that other metal carbonyls can photodissociate under $d \rightarrow \pi^*$(CO) excitation, it does demonstrate that the long-standing postulation that only LF excited states can initiate the release of CO is not generally valid.

Upon irradiation of Ni(CO)$_4$ in an inert gas matrix at 15°K the formation of a nonplanar ($C_{3v}$) Ni(CO)$_3$ fragment was observed.[110] A partial recombination of the released CO ligand with Ni(CO)$_3$ was achieved when the matrix was warmed to 30°K. The photolysis of Ni(CO)$_4$ in a nitrogen

matrix at $20°K$ led to the formation of $Ni(CO)_3N_2$.[111] Investigations of the decomposition of $Ni(CO)_4$ by gas-phase flash photolysis gave results that were consistent with the formation of $Ni(CO)_3$ and $Ni(CO)_2$ intermediates.[112] The decomposition was inhibited by added CO. This inhibition is probably due to the reversal of the photolysis. Photochemical substitution reactions of $Ni(CO)_4$ have not yet been investigated. This deficiency is probably associated with the fact that thermal substitutions of $Ni(CO)_4$ are generally fast.[1-3] The thermal lability of Ni—CO bonds may be related to the occupation of the antibonding $t_2$ orbitals in the ground state of $Ni(CO)_4$.

## VIII. PHOTOISOMERIZATION OF COORDINATED OLEFINS

The photochemical *trans-cis* isomerization of coordinated olefins has been observed for a variety of carbonyl complexes. In all cases, it is likely that orbitals of the olefin are involved in the electronic transition initiating the transformation of the olefinic ligand. Generally, two different situations may lead to the observed isomerizations, which require a free or less hindered rotation around the olefinic double bond. First, the double bond may be weakened by removal of an electron from a $\pi$-bonding orbital of the olefin. This may be achieved by $\pi$-to-$\pi^*$ intraolefin, $\pi$(olefin)-to-metal CT and $\pi$(olefin)-to-$\pi^*$(CO) CT transitions. Second, the double bond may be weakened by placing an electron into the antibonding $\pi^*$ orbital of the olefin. This occurs in $\pi$-to-$\pi^*$ intraolefin, metal-to-$\pi^*$(olefin) CT, and $\pi$- or $\sigma$(CO)-to-$\pi^*$(olefin) CT transitions.

Although reliable assignments of electronic absorption bands of these olefin complexes have not yet been reported, rough estimates can be made since the ionization potentials and the energies of the lowest $\pi \rightarrow \pi^*$ transitions of many olefins are known.[113,114] It seems likely that low-energy transitions of olefin-metal-carbonyl complexes involving $\pi$ orbitals of the olefin are possible. In addition, it is also feasible that the isomerization does not take place at the coordinated olefin. The electronically excited complex may dissociate into a metal-carbonyl fragment in its ground state and the olefin in an excited state. The lowest excited triplet of many olefins is known to lead to *cis-trans* isomerizations.[115] Such a mechanism would require that the lowest triplet of the olefin is lower than the initially excited state of the complex. The isomerized olefins may then recombine with the complex fragment.

Photoisomerization of coordinated *trans-* and *cis*-stilbene was observed for $Mo(CO)_5$stilbene and $W(CO)_5$stilbene; the M(CO)$_5$L compounds were produced by photolysis of the hexacarbonyls in the presence of the olefins.[116] Starting with either *trans-* or *cis*-stilbene, a photostationary state was reached. The photocatalysis by $W(CO)_6$ led to an equilibrium of about 40% *trans-* and 60% *cis*-stilbene. It was shown that the

isomerization probably takes place at the coordinated olefin. Absorption of light was limited to the long-wavelength band ($\lambda_{max} \sim 415$ nm) of the complex. Neither the hexacarbonyls nor the free stilbenes absorb in this region. The overall quantum yields were of the order of 0.01.

Although no assignment was made for the long-wavelength band of these olefin complexes, low-energy $d-\pi^*$(stilbene) CT transitions should be possible. Such transitions may weaken the olefinic double bond and facilitate the isomerization. It was proposed that the excited state of the complex produces an intermediate characterized by a metal-carbon $\sigma$-bond with free rotation about the olefin bond. Intermediates of this type were suggested to result from metal-to-olefin CT excitation that leads to a positively charged metal carbonyl fragment and an olefin anion.[7,114] This nucleophilic radical anion may then attack the metal to form a metal-carbon $\sigma$-bond in the transition state.[114] Hence the regeneration of the starting complex proceeds under isomerization of the olefin. Cr(CO)$_6$ was found to be inactive in the photocatalysis of stilbene isomerization.[116] This result was explained as being due to the large difference in the ability of the three metals to bind the olefin. In addition, the photoactive excited state was assumed to be not a singlet, but a triplet that may not be populated in the chromium complex because of the smaller probability of spin-forbidden transitions. However, this latter explanation should be accepted with reservation since there is some evidence that intersystem crossing from the lowest singlet excited state to the lowest triplet of Cr(CO)$_6$ occurs with unit efficiency.[20] Alternatively, the inability of Cr(CO)$_6$ to photocatalyze the isomerization of stilbene may be due to smaller $d-d$ splittings in chromium compared to molybdenum or tungsten complexes.[11] If the $d\sigma$ levels are lower in energy than the $\pi^*$(stilbene) states, the irradiation of the complex could lead to LF excited states that may not initiate the isomerization.

Irradiation of W(CO)$_6$ in the presence of 1,3-pentadiene or 2,4-hexadiene led to *cis-trans* isomerizations of the conjugated dienes with quantum yields being smaller than 0.1 at 313 nm irradiating wavelength.[117] The lowest triplet excited state of W(CO)$_5$diene was assumed to be the precursor of the photoisomerization. Although *cis*-to-*trans* was preferred over *trans*-to-*cis* isomerization, as is also the case for the free diene in its lowest triplet excited state, the intermediate formation of an excited free diene was ruled out for the isomerization photocatalyzed by W(CO)$_6$.

*Trans*-to-*cis* photoisomerization of coordinated olefins was also observed for W(CO)$_5$(*trans*-4-styrylpyridine) and W(CO)$_5$(*trans*-2-styrylpyridine).[38] In contrast to the complexes discussed above, the styrylpyridines, NC$_5$H$_4$—CH=CH—C$_6$H$_5$, are assumed to be coordinated via nitrogen instead of the olefinic double bond. The longest wavelength

absorption of these complexes was assigned to the lowest LF transition in analogy to other N-coordinated $W(CO)_5$ complexes. The quantum yield of isomerization of the olefin increased with increasing wavelength and was highest upon irradiation of the longest wavelength band of the complex [$\phi = 0.49$ at 436 nm for $W(CO)_5$(*trans*-4-styrylpyridine)]. In addition, a photosubstitution of the olefinic nitrogen base by 1-pentene was observed with quantum yields that also increased with increasing wavelength of irradiation [$\phi = 0.16$ at 436 nm for $W(CO)_5$(*trans*-4-styrylpyridine)]. It was assumed that higher excited states of the complex undergo internal conversion to the lowest LF excited state that initiates the photosubstitution. Since, however, the lowest triplets of the free styrylpyridines known to lead to *trans-cis* isomerizations have presumably lower energies ($\sim 50$ kcal) than the lowest LF triplets of the complexes (58 kcal), it was suggested that the photoisomerization of the coordinated ligand takes place by transfer of a large portion of the excitation energy from the complex to the olefin. Additional evidence for an efficient energy transfer to the olefin was obtained by the observation that these complexes did not show any emission from their lowest LF triplet states. However, the low energies of the $\pi-\pi^*$ transitions of the styrylpyridines and the perturbation of the $\pi$-electron system upon coordination, which is indicated by a significant shift of the $\pi-\pi^*$ absorption of free *trans*-4-styrylpyridine (255 nm) to lower energies in the coordinated state (316 nm), do not exclude that $d-\pi^*$(olefin) CT contributes to the lowest energy transition of these complexes. Then it would not be necessary to invoke energy transfer to an intraolefin excited state as explanation for the observed photoisomerization.

*Cis-trans* photoisomerizations of coordinated olefins are not limited to carbonyls of Mo and W. Irradiation of dimethyl maleate iron tetracarbonyl yielded dimethyl fumarate iron tetracarbonyl.[7,114,118] This *cis*-to-*trans* isomerization was assumed to be initiated by a metal-to-$\pi^*$(olefin) CT transition. However, the efficiency of this isomerization seems to be small, whereas the dimethyl maleate ligand was photoexchanged with labeled dimethyl maleate with quantum yields between 0.27 and 0.47. It was suggested that the initially excited CT state may undergo an efficient internal conversion to a lower LF excited state, which causes the release of the equatorial olefinic ligand without isomerization. The first-order kinetics of this photoexchange is consistent with the intermediate formation of a $Fe(CO)_4$ fragment. The same type of photoexchange was observed for dimethyl fumarate and methyl acrylate iron tetracarbonyl.

Irradiation of either (*cis*-CHBr═CHBr)Fe(CO)$_4$ or (*trans*-CHBr═CHBr)Fe(CO)$_4$ led to an intramolecular insertion of iron into one of the carbon-bromine bonds of the coordinated olefin to yield

$(CO)_4BrFe$—$CH$=$CHBr$ as primary photoproduct.[114] Since the iron was shown to be *trans* to the bromine of the $\sigma$-bonding —$CH$=$CHBr$ ligand, a rotation about the olefinic double bond must have occurred in the case of ($cis$-$CHBr$=$CHBr$)$Fe(CO)_4$ as starting complex. It was concluded that these insertion reactions originate from $d$–$\pi^*$(olefin) CT transitions; they were assigned to the lowest energy absorptions in the electronic spectra of ($cis$- and $trans$-$CHBr$=$CHBr$)$Fe(CO)_4$. Since the $\pi^*$ level of $CHBr$=$CHBr$ is antibonding for both the C—C and C—Br bonds as well, the CT excited state was assumed to facilitate free rotation about the olefinic bond and insertion of the positively charged iron into a C—Br bond by a nucleophilic attack of the olefinic radical anion.

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