Photochemical investigations of organometallic compounds—those which contain at least one direct metal-carbon bond—have been fewer than those of classical inorganic coordination compounds. However, this situation is changing rapidly, in part because of the demonstrated importance of this area of chemistry since organometallic compounds have proven extremely useful reagents for catalyzing or assisting a large number of organic transformations. Organometallic compounds obey exactly the same laws of photochemistry and photophysics as do the coordination compounds discussed in the preceding articles in this issue, and exactly analogous photochemical techniques are employed in their study. However, consideration must often be given to the air-sensitivity of some organometallic compounds and also to their different solubility properties—many organometallics are soluble in hydrocarbon solvents but few dissolve in water. There are many different classes of organometallic compounds containing carbonyl, allyl, olefin, arene, cyclopentadienyl, hydride, etc. ligands, and it is not possible to discuss all of these in this single article. The interested reader is referred on photochemistry (2). By far the largest number of organometallic photochemical studies have involved metal carbonyl complexes and we begin with a discussion of their photosubstitution chemistry.

Photosubstitution of Metal Carbonyl Complexes

The dominant photochemical reaction of metal carbonyl derivatives is carbon monoxide loss, generally followed by substitution of another ligand for the expelled CO. Representative examples of such photochemistry are set out in eqns. (1)–(7).

\[ V(\eta^5-C_6H_5)(CO)_4 + PhC==CPh \rightarrow V(\eta^5-C_6H_5)(CO)_3(PhC==CPh) + CO \] (1)

\[ W(CO)_3 + PPh_3 \rightarrow W(CO)_3(PPh_3) + CO \] (2)

\[ Mo(\eta^6-mesitylene)(CO)_3 + C_2H_4 \rightarrow Mo(\eta^6-mesitylene)(CO)_2(C_2H_4) + CO \] (3)

\[ ReCl(CO)_5 + pyridine \rightarrow ReCl(CO)_4(pyridine) + CO \] (4)

\[ Fe(CO)_3 + 1,3-butadiene \rightarrow Fe(CO)_2(1,3-butadiene) + 2 CO \] (5)

\[ Co(CO)_3NO + PF_3 \rightarrow Co(CO)_{3-x}(NO)(PF_3)_x + xCO \] (6)

(where \( x = 1, 2, 3 \))

\[ Rh(\eta^5-C_6H_5)(CO)_2 + R_3SiH \rightarrow Rh(\eta^5-C_6H_5)(CO)(H)(R_3Si) + CO \] (7)

As illustrated by these examples, photosubstitution of CO by ligand L in metal carbonyl complexes is an extremely useful synthetic procedure for preparing metal carbonyl derivatives, and a wide variety of substituting ligands can be used. The metal carbonyls themselves, or simple derivatives of them such as \( V(\eta^5-C_6H_5)(CO)_4 \), can usually be prepared directly from inorganic starting reagents or, more customarily, can be purchased directly from chemical supply houses. The subsequent transformation of these into other derivatives can be effected by thermal or photochemical means, but the photochemical substitution route can be carried out at room temperature or below, thereby avoiding the use of high temperatures which may lead to decomposition of unstable ligands and complexes.

Such preparative reactions are often best carried out by first irradiating the complex in a weakly coordinating solvent such as acetone, acetonitrile, pyridine, or most often tetrahydrofuran (THF) to prepare a solvent-substituted derivative and then, in a subsequent thermal substitution, replacing the solvent ligand with the desired ligand. A particular case where this has been often used is with \( Mn(\eta^5-C_6H_5)(CO)_3 \), eqns. (8) and (9).

\[ Mn(\eta^5-C_6H_5)(CO)_3 + THF \rightarrow Mn(\eta^5-C_6H_5)(CO)_2(THF) + CO \] (8)

\[ Mn(\eta^5-C_6H_5)(CO)_3(THF) + L \rightarrow Mn(\eta^5-C_6H_5)(CO)_3L + THF \] (9)

The solvent ligand is usually readily displaced at room temperature or slightly above and thus high temperatures are not required. The advantages of preparing the solvent-substituted complex first are that such reactions can usually be driven to essentially 100% completion because of the high entering ligand concentration and that secondary photoreactions, for example substitution of a second CO ligand, are generally not a serious problem.

An important question is—why does photoexcitation so generally lead to dissociation of a CO ligand (3)? Simple one-electron arguments can be used to understand the excited state stabilization in much the same way that \( \pi \rightarrow \pi^* \) excited states of olefins are rationalized to undergo cis-trans isomerization; depopulation of the \( \pi_2 \) level and population of the \( \pi^* \) reduces the C—C bond order to yield essentially a single
carbon-carbon bond having little barrier to rotation. In metal complexes, it is the \( d \) orbitals that are involved in the \( \sigma \) and \( \pi \) bonding between the metal and ligands, and the effects of photochemical excitation upon the relative population of these must be considered. For the \( d^6 \) metal hexacarbonyl complexes, e.g., \( \text{M(CO)}_6 \) (M = Cr, Mo, W), the orbital and state diagrams shown in Figure 1 are appropriate. The \( d_{2g} \) and \( d_{2g}\overline{2} \) orbitals of \( e_g \) symmetry are antibonding (\( \sigma^* \)) with respect to the metal-ligand sigma interactions whereas the \( d_{xy}, d_{yz}, \) and \( d_{xz} \) orbitals of \( t_{2g} \) symmetry are weakly \( \pi \)-bonding between the metal and the CO ligands. The lowest-lying excited states in these \( \text{M(CO)}_6 \) complexes have been assigned as ligand field states arising from \( t_{2g}(\pi) \rightarrow e_g(\sigma^*) \) transitions—specifically, the \( ^1A_{1g} \rightarrow ^1T_{1g}, ^1T_{2g} \) transitions indicated in Figure 1. The \( ^1T_{1g} \) state lies lowest and is generally believed to be the excited state from which CO loss occurs. These transitions involve depopulation of a metal-ligand bonding orbital and population of an orbital that is strongly antibonding between the ligands and the metal. Thus, the metal-ligand bonding is greatly weakened in the excited state, and CO loss is the anticipated and observed result.

The \( d^6 \) metal hexacarbonyls that have been studied are extremely photosensitive with respect to dissociative loss of CO. It is interesting that the \( t_{2g} \rightarrow e_g \) type one-electron excitation results in such extreme labilization. Let us assume that the ground and excited state substitution of the metal hexacarbonyl proceeds by a dissociative-type mechanism involving the generation of a pentacarbonyl species, an assumption that is supported by numerous experimental results. Then what is the excited state dissociation rate constant compared to the ground state? Given that 1) the ground state rate constant can be in the range \( 10^{-9} \) sec\(^{-1} \); 2) the excited state lifetime is known to be \(<10^{-10} \) sec; and 3) virtually every metal hexacarbonyl which is excited produces the pentacarbonyl, the excited state dissociation constant can be estimated to be \( \approx 10^{10} \) sec\(^{-1} \), some 16 orders of magnitude greater than for the ground state.

An important question is whether the extreme increase in ligand lability is due predominantly to depopulation of \( \pi \)-bonding levels or to population of the \( \sigma \)-antibonding levels; or whether both contribute substantially. Both obviously contribute, but it does appear that the population of the \( \sigma \)-antibonding levels is most important. This can be appreciated by realizing that \( d^6 \) \( \text{V(CO)}_6 \), which has one of the \( t_{2g} \) orbitals already depopulated in its ground state, is relatively substitution-inert. However, \( d^6 \) \( \text{V(CO)}_6^- \) is photosubstitution-labile upon \( t_{2g} \rightarrow e_g \) type excitation, implying that it is population of the \( e_g \)-antibonding orbitals that leads to the greatest degree of M–CO bond weakening.

Similar excited state arguments can be applied to other lower-symmetry metal carbonyl complexes to rationalize observed CO loss upon photoexcitation. It should, however, be noted that the quantum yield of CO loss generally decreases as complexes become more highly substituted, often to the point of becoming essentially nonobservable. Thus, although Fe(CO)\(_5\) loses CO with a high quantum yield, Fe(CO)\(_5\)(PPh\(_3\))\(_2\) does not appear to lose CO at all upon excitation, and PPh\(_3\) dissociation occurs instead. In a qualitative sense, it can be argued that as CO ligands are progressively replaced in a metal-carbonyl complex, the bonding between the metal and the remaining CO ligands becomes progressively stronger, and thus these CO ligands are not easily dissociated even by photochemical means.

These results also have an excited state basis, as illustrated by the orbital diagrams shown in Figure 2 which compares the \( d \)-level splitting in an octahedral \( \text{M(CO)}_6 \) complexes with a substituted \( \text{M(CO)}_5 \text{L} \) complex. If \( L \) is lower in the chemical series than CO, then the octahedral \( e_g \) orbitals will split such that \( d_{2g} \) will lie lower than \( d_{2g}\overline{2} \). The lowest lying ligand-field excited state will then derive from \( \tau \rightarrow \tau \) excitations, and the principal antibonding M–L interaction will be localized along the \( z \) axis, a result that would predict photochemical labilization of either the ligand \( L \) or the CO ligand which lie upon the \( z \) axis, eqns. (10) and (11).

\[
\text{M(CO)}_5L \xrightarrow{h\nu} \text{M(CO)}_5 + L \tag{10}
\]

\[
\text{M(CO)}_5L \xrightarrow{h\nu} \text{M(CO)}_5L + \text{CO} \tag{11}
\]

The relative efficiencies of processes (10) and (11) have been found to be very sensitive to the nature of \( L \). For certain \( L \) ligands, such as tetrahydrofuran, process (11) is insignificant and essentially complete conversion of \( \text{M(CO)}_5 \) into \( \text{M(CO)}_5(\text{THF})_2 \) can occur without competition arising from process (11) which would lead to a substituted \( \text{M(CO)}_5(\text{THF})_2 \) complex. The relative importance of reaction (11) has generally been found to increase with increasing strength of the M–L bond. It is not obvious that such a correlation should exist since the excitation energies are high enough to yield loss of either CO or L. If a common excited state is responsible for both reactions (10) and (11), the correlation can be rationalized by merely assuming that photoexcitation causes the same relative increase in the substitution rates for both L and CO. In such a case, comparison of ground state binding strength may yield the correlation observed: when L and CO are more comparable in binding strength, release of CO is competitive with release of L, even though in the ground state both undergo substitution slowly. Thus, when L resembles CO in its bonding properties, sequential substitution of CO by L is possible until every CO has been replaced; e.g., [\( \text{Mo(CO)}_5 \text{L} \)] can be converted entirely to [\( \text{Mo(P(OCH}_3)_3 \text{L}) \)] by photolysis in the presence of excess \( \text{P(OCH}_3)_3 \) (4).

A second parameter also affects the relative efficiencies of reactions (10) and (11). The quantum yield for reaction (11) for photosubstitution of pyridine (py) for CO in \( \text{M(CO)}_5(\text{py}) \) complexes was found to be sensitive to the wavelength of the exciting light, as evidenced by data like those shown in Table 1 (5). Higher energy irradiation yields more efficient loss of CO. Such an effect can be attributed to at least two reactive excited states or to differences in the reactivity of one excited state depending on the vibrational level directly achieved. The latter alternative is not likely since the reactions are carried out in condensed media where rapid vibrational relaxation should occur. Other data have shown that both reactions (10)
Table 1. Wavelength Dependence for Quantum Efficiency of [M(CO)₅(Pyridine)] to [M(CO)₄(Pyridine)]₂ Conversion a

<table>
<thead>
<tr>
<th>Central Metal</th>
<th>Solvent</th>
<th>Φ₃96 nm</th>
<th>Φ₴₃₆ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>CsH₅</td>
<td>0.21</td>
<td>0.13</td>
</tr>
<tr>
<td>Cr</td>
<td>THF</td>
<td>0.28</td>
<td>0.17</td>
</tr>
<tr>
<td>Mo</td>
<td>CsH₅</td>
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</tr>
<tr>
<td>Mo</td>
<td>THF</td>
<td>0.35</td>
<td>0.22</td>
</tr>
<tr>
<td>W</td>
<td>CsH₅</td>
<td>0.11</td>
<td>0.08</td>
</tr>
<tr>
<td>W</td>
<td>THF</td>
<td>0.06</td>
<td>0.02</td>
</tr>
</tbody>
</table>

* Data from reference (5).

Table 2. Quantum Yield Data for Photosubstitution of L in W(CO)₅L a

<table>
<thead>
<tr>
<th>L</th>
<th>438 nm</th>
<th>514 nm</th>
<th>Lowest Excited State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyridine</td>
<td>0.62</td>
<td></td>
<td>LF</td>
</tr>
<tr>
<td>3-Acetylpyridine</td>
<td>0.75</td>
<td></td>
<td>LF</td>
</tr>
<tr>
<td>3,5-Dibromopyridine</td>
<td>0.62</td>
<td></td>
<td>W → L CT</td>
</tr>
<tr>
<td>4-Benzoylpyridine</td>
<td>0.12</td>
<td>0.02</td>
<td>W → L CT</td>
</tr>
<tr>
<td>4-Formylpyridine</td>
<td>0.05</td>
<td>0.002</td>
<td></td>
</tr>
</tbody>
</table>

* Data taken from reference (7).

Figure 3. Correlation of excited state and observed reactivity for [W(CO)₅(pyridine)].

and (11) for M(CO)₅(py) are wavelength-dependent, with reaction (10) having less importance upon higher excitation energy (6). The opposite wavelength dependence for these two processes can be rationalized by invoking two different reactive LF excited states, as detailed in Figure 3. Low-energy excitation yields population of the dₓᵧ(σₓᵧ*) orbital with σ antibonding character directed principally along the z axis, strongly labilizing the σ donor, pyridine, and also the axial CO. Higher energy excitation populates the dₓ₋ₓᵧ(σₓ₋ₓᵧ*) orbital with strong labilizing effects for the equatorial CO ligands. Internal conversion of the upper state to the lower state with rate constant kᵣᵤ adequately accounts for the fact that reaction (10) also occurs upon high-energy excitation.

The photosubstitution efficiency of either pyridine or CO in substituted W(CO)₅L (L = pyridine or substituted pyridine) complexes, can also be markedly altered by changing the pyridine substituents, which has the effect of changing the character of the lowest-lying excited states (7). Some representative data are given in Table 2 for photosubstitution of 1-pentene for L, eqn. (12)

W(CO)₅L + 1-pentene → W(CO)₅(1-pentene) + L (12)

For those complexes which have ligand field (LF) states lying lowest in energy, as illustrated on the left of Figure 4, photosubstitution of the ligand L occurs with high quantum efficiency. However, for those complexes which have the W → L charge transfer excited state lying lowest, as indicated on the right of Figure 4, photosubstitution occurs with greatly attenuated efficiency and is essentially insignificant when irradiation is directly into the W → L CT band (λ = 514 nm). This data clearly shows the important role of ligand-field excited states in photosubstitution chemistry.

Photoinduced Cleavage of Metal-Metal Bonds

A set of compounds which illustrate particularly well the effect of the nature of the lowest-lying excited state on the photoreactivity are the metal carbonyl dimers such as Mn₂(CO)₁₀.

Following the examples presented in the preceding section, one might naively anticipate that photolysis of such compounds would also induce CO loss and lead to photosubstitution chemistry. However, it is instructive to first consider an orbital diagram for such complexes. Of the metal-metal bonded dinuclear complexes, Mn₂(CO)₁₀ is the cornerstone example, and its electronic structure can be rationalized according to Figure 5 (8). Each of the Mn(CO)₅ fragments has square pyramidal C₄ᵥ symmetry with a d⁷ electronic config-
urariun, and the orbital orderings on the sides of Figure 5 are appropriate. In forming the dimeric complex, the $d_{z^2}$ orbitals on each fragment overlap to give metal-metal bonding ($\sigma_b$) and metal-metal antibonding ($\sigma^*$) orbitals. The bonding orbital is occupied by a pair of electrons, but the $\sigma^*$ orbital is empty in the ground state, giving a net single bond between the two metal atoms. The $d\pi$ orbitals ($d_{xz}$, $d_{yz}$, $d_{xy}$) are essentially localized on each metal fragment and do not appreciably interact.

The electronic absorption spectra of $\text{Mn}_2(\text{CO})_{10}$ and two $\text{PPh}_3$-substituted derivatives are illustrated in Figure 6 (9). $\text{Mn}_2(\text{CO})_{10}$ shows two low-lying absorption features: a low energy shoulder at 375 nm (26,700 cm$^{-1}$) on an intense band at 336 nm (29,740 cm$^{-1}$, $\epsilon = 33,700$ M$^{-1}$ cm$^{-1}$). Consideration of the orbital diagram in Figure 5 leads to the prediction of the two lowest-lying transitions arising from $d\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ excitations. Of these, the $d\pi \rightarrow \sigma^*$ band is symmetry-forbidden and should be of low intensity whereas the $\sigma \rightarrow \sigma^*$ band is fully allowed. The less intense shoulder in the spectrum of $\text{Mn}_2(\text{CO})_{10}$ has been assigned as the $d\pi \rightarrow \sigma^*$ transition and the intense 336 nm band is attributed to the $\sigma \rightarrow \sigma^*$ transition (8, 9). A large number of homodinuclear and heterodinuclear metal-metal bonded complexes exhibit a near-ultraviolet absorption band like that for $[\text{Mn}_2(\text{CO})_{10}]$. Indeed, a $\sigma \rightarrow \sigma^*$ absorption is observed for any system where it is appropriate to consider the metal-metal bond as resulting from the coupling of two 17-electron fragments giving a diamagnetic, two-electron metal-metal bonded species. Such is the case for metal-metal bonded dinuclear complexes resulting from any combination of $[\text{Co}(\text{CO})_4]$, $[\text{Re}(\text{CO})_5]$, $[\text{Mn}(\text{CO})_5]$, $[\text{Fe}(\tau^5-\text{C}_5\text{H}_5)(\text{CO})_2]$, $[\text{Mo}(\tau^5-\text{C}_5\text{H}_5)(\text{CO})_2]$, $[\text{W}(\tau^5-\text{C}_5\text{H}_5)(\text{CO})_2]$, etc.

Given that the low-lying electronic transitions in single metal-metal bonded dimers are of the $d\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ type, what sort of photochemistry might be expected for such compounds? Both of these transitions populate the metal-metal antibonding orbital and certainly the metal-metal bonding should be greatly weakened. The $\sigma \rightarrow \sigma^*$ transition in particular yields an excited state with zero net bonding between the two mononuclear metal centers, and thus the prediction is that photolysis of such compounds should lead to rupture of the metal-metal bond and formation of two 17-electron metal fragments.

Indeed, such a reaction does dominate the photochemistry of single metal-metal bonded dinuclear carbonyl complexes, as illustrated in eqn. (13) for $\text{Mn}_2(\text{CO})_{10}$.

$$\text{(CO)}_5\text{Mn-Mn} \rightarrow \text{(CO)}_5\text{Mn} + \text{Mn}$$

The 17-electron metal fragments display radical-like reactivity, and, for example, readily abstract halide ligands from halocarbon solvents, eqn. (14).

$$\text{Mn}_2(\text{CO})_{10} \rightarrow \text{2Mn(CO)}_5\text{Cl}$$

Under 313 nm irradiation, the quantum yield of disappearance of $\text{Mn}_2(\text{CO})_{10}$ in $\text{CCl}_4$ solution is 0.48 and, as expected, the quantum yield for formation of $\text{Mn}(\text{CO})_5\text{Cl}$ is essentially twice that, 1.02 (9). The metal fragments produced upon photolysis of single metal-metal bonded complexes have also been shown to react with $\text{I}_2$ to give mononuclear iodide complexes

$$\text{Re}_2(\text{CO})_{15} \rightarrow \text{2Re(CO)}_5\text{I}$$

and have been detected by flash photolysis experiments and by ESR spectroscopy using spin traps (9). The flash photolysis experiments indicate that the metal fragments recombine in inert solvents in the absence of suitable scavengers at nearly diffusion-controlled rates. Other evidence for photoinduced homolysis of single metal-metal bonds includes the formation of ESR-detectable Ph$_3$C- radicals upon photolysis of $\text{W}_2(\tau^5-\text{C}_5\text{H}_5)(\text{CO})_2$ in the presence of Ph$_3$CCI

$$\text{(CO)}_5\text{W-W(CO)}_5(\tau^5-\text{C}_5\text{H}_5)$$

and photolysis of the same compound in the presence of benzoylchloride to give dibenzyl in high yield (10).


\[(\eta^1-C_2H_5)(CO)W-W(\eta^1-C_2H_5)(CO)_2 \xrightarrow{h\nu} \]

\[2 \cdot W(\eta^1-C_2H_5)(CO)_3 + 2 \text{PhCH}_2\text{Cl} \]  \hspace{1cm} \text{(17)}

Irradiation of \(W_2(\eta^1-C_2H_5)_2(CO)_6\) in various halocarbons has given the following ordering of reactivity with the photogenerated \(-W(CO)_5(\eta^1-C_2H_5)\) fragments: \(\text{CCl}_4 > \text{CHCl}_3 > \text{PhCH}_2\text{Cl} > \text{CH}_2\text{Cl}_2\) (17).

One of the most compelling pieces of evidence for photoinduced homolytic cleavage of single metal-metal bonded complexes are the metal exchange reactions which can be induced. Several examples are given in eqns. (18) and (19).

\[\text{Re}_2(\text{CO})_{10} + \text{Mn}(\text{CO})_{10} \xrightarrow{h\nu} 2\text{MnRe}(\text{CO})_{10} \] \hspace{1cm} \text{(18)}

\[M_2(\eta^1-C_2H_5)_2(CO)_2M' + \text{M}''(\text{CO})_{10} \xrightarrow{h\nu} M = \text{Mo}, W \] \hspace{1cm} \text{(19)}

These reactions presumably proceed via photoinduced homolysis of the metal-metal bonds followed by subsequent cross-coupling of the resultant 17-electron metal complexes. Such a reaction necessarily gives an equilibrium mixture of products; the position of this equilibrium will depend upon the quantum yield of homolysis of each of the compounds involved as well as their absorptivity at the wavelength of irradiation. Furthermore, as indicated in eqns. (18) and (19), the equilibrium can be approached from either direction beginning with the homometallic dimers or the mixed-metal compounds. This type of photochemical reaction has been widely exploited for the synthesis of particularly desired mixed-metal dinuclear complexes and in many cases is better than other synthetic methods (17-19). In general it can be expected that irradiation of any pair of single metal-metal bonded dinuclear complexes will lead to formation of the cross-coupled products.

Interesting mechanistic experiments can be conducted for this type of photoreaction. For example, if an \(M-M'\) bonded species is irradiated in the presence of a halogenated solvent, then the relative efficiencies of reactions such as (20) and (21) can be determined.

\[2(\eta^1-C_2H_5)(CO)_3M-M'(CO)_5 \xrightarrow{h\nu} \]

\[M_2(\eta^1-C_2H_5)_2(CO)_2 + \text{M}''(\text{CO})_{10} \] \hspace{1cm} \text{(20)}

\[M_2(\eta^1-C_2H_5)(CO)_3(CO)Cl + \text{M}''(\text{CO})_5 \xrightarrow{h\nu} \]

\[\text{ClM}(\eta^1-C_2H_5)(CO)_3 + \text{ClM}(\text{CO})_5 \] \hspace{1cm} \text{(21)}

In such a case it has proven possible to determine the relative reactivity of the \(M\) and \(M'\) centered radicals toward a given halogen donor, and, furthermore, if \(M-M'\) bonded species are irradiated in the presence of two different halogen donors, the relative reactivity of the two donors can be obtained (15). Such studies have been used to establish that the electronic structure of the photogenerated \([\text{Mo}(\eta^1-C_2H_5)(CO)_5]\) radical is independent of its source; that is, the photogenerated radicals from a series of metal-metal bonded complexes involving the \([\text{Mo}(\eta^1-C_2H_5)(CO)_5]\) unit give a species with the same properties toward two halocarbons. Second, the reactivity of a series of metal-centered radicals toward \(\text{CCl}_4\) and 1-iodopentane show the following ordering: \([\text{Re}(\text{CO})_5] > [\text{Mn}(\text{CO})_5] > [\text{W}(\eta^1-C_2H_5)(CO)_5] > [\text{Mo}(\eta^1-C_2H_5)(CO)_5] > [\text{Fe}(\eta^1-C_2H_5)(CO)_5] > [\text{Co}(\eta^1-C_2H_5)(CO)_5]\).

Although photolysis of single metal-metal bonded binuclear complexes leads predominately to metal-metal bond homolysis, photosubstitution of CO can also be affected by irradiation in the presence of added ligand L, e.g., eqn. (22).

\[\text{Mn}_2(\text{CO})_{10} + \text{FPPh}_3 \xrightarrow{h\nu} \]

\[\text{Mn}_2(\text{CO})_{9}(\text{FPPh})_3 + \text{Mn}_2(\text{CO})_{9}(\text{FPPh})_2 \] \hspace{1cm} \text{(22)}

A variety of entering \(L\) ligands have been employed in such reactions ranging from substituted phosphorus ligands to nitrides to olefins and even \(\text{H}_2\text{O}\). However, the available evidence indicates that these photosubstitution reactions also proceed through initial light-induced metal-metal bond cleavage, as outlined in eqn. (23) (1, 9).

\[\text{Mn}_2(\text{CO})_{10} \xrightarrow{h\nu} \]

\[2[\text{Mn}(\text{CO})_4] + \text{FPPh}_3 \rightarrow 2[\text{Mn}(\text{CO})_4] + \text{FPPh}_3 + 2\text{CO} \] \hspace{1cm} \text{(23)}

\[\text{Mn}_2(\text{CO})_{9}(\text{FPPh})_3 + \text{Mn}_2(\text{CO})_{9}(\text{FPPh})_2 \]

Seventeen-electron metal fragments such as \(\text{Mn}(\text{CO})_5\) have been demonstrated to be very substitution labile, although there is some discussion as to whether such reaction proceeds by a dissociative or associative pathway. In any case, the photogenerated \([\text{Mn}(\text{CO})_5] \) fragments can undergo substitution of \(L\) for \(\text{CO}\) and then recombination of the radical fragments leads to the substituted dinuclear complexes. Support for this mechanism comes from the observation that \(\text{Mn}_2(\text{CO})_9(\text{FPPh})_2\) is the major primary photoprodut in eqn. (22) with the monosubstituted \(\text{Mn}_2(\text{CO})_9(\text{FPPh})_2\) compound a minor (~5%) component of the product mixture. If the usual mechanism of photosubstitution were operating, that involving simple photoinduced loss of \(\text{CO}\) from \(\text{Mn}_2(\text{CO})_{10}\) to give \(\text{Mn}_2(\text{CO})_9\) as the intermediate, then \(\text{Mn}_2(\text{CO})_9(\text{FPPh})_2\) should be the principal product at short irradiation times, but this is not observed.

Thus, we have the general results that photolysis of mononuclear metal carbonyl complexes usually leads to photodissociation of \(\text{CO}\) whereas photolysis of dinuclear metal carbonyl complexes commonly gives metal-metal bond cleavage. An interesting question concerns whether photolysis of polynuclear cluster complexes, such as \(\text{Ru}_4(\text{CO})_{12}\) and \(\text{H}_2\text{FeRu}_3(\text{CO})_{12}\), will give metal-metal bond cleavage or photodissociation of \(\text{CO}\) in their primary photochemical reactions.

The electronic absorption spectra of such cluster compounds imply that the lowest-lying electronic transitions are localized within the metal fragment and likely involve either depopulation of metal-metal bonding orbitals or population of the corresponding antibonding orbitals, or both. Thus photoinduced metal-metal bond cleavage might be the expected result. However, it is unlikely that absorption of a single photon could induce cleavage of more than one metal-metal bond, and the remaining framework bonds could be sufficient to maintain the compound’s integrity. Thus, fragmentation reactions might not be observed.

Only a few photochemical studies of clusters have been conducted, but with trinuclear complexes, photoinduced fragmentation has been seen. Thus, \(\text{H}_2\text{Re}_3(\text{CO})_{12}\) was shown
to convert smoothly and quantitatively into H₂Ru₂(CO)₆ upon photolysis, eqn. (24) (14),

\[ 2 \text{H}_2\text{Re}_2(\text{CO})_{12} \xrightarrow{hv} 3 \text{H}_2\text{Re}_2(\text{CO})_{6} \]  

(24)

and the binuclear Mn(CO)₁₂ (M = Fe, Ru) clusters have been known to photofragment for some time (1, 15), e.g., eqn. (25).

\[ \text{Ru}_{2}(\text{CO})_{12} + \text{PPh}_3 \xrightarrow{hv} \text{Ru}(\text{CO})_3(\text{PPh}_3)_2 + \text{Ru}(\text{CO})_4(\text{PPh}_3) + \text{CO} \]  

(25)

However, Os₃(CO)₁₂ is resistant to fragmentation and instead undergoes CO photosubstitution with a low quantum yield, eqn. (26) (16).

\[ \text{Os}_3(\text{CO})_{12} + \text{PPh}_3 \xrightarrow{hv} \text{Os}_3(\text{CO})_{11}(\text{PPh}_3) + \text{CO} \]  

(26)

The exact nature of the photofragmentation pathways of these trinuclear clusters has not been clearly defined. Based on analogy to the binuclear metal-metal bond cleavage reactions discussed above, it was initially suggested that photolysis of Ru₃(CO)₁₂ leads first to the diradical intermediate I in eqn. (27) which rapidly reacts with added ligand L to give photoproducts (17). However, other workers have instead favored a spin-paired intermediate such as II which can undergo ligand addition at the coordinatively-unsaturated Ru(CO)₃ center and then subsequent fragmentation (18).

\[ \begin{array}{c}
\text{Ru}_{3}(\text{CO})_{12} \xrightarrow{hv} \text{Ru}(\text{CO})_3 \xrightarrow{L} \text{Ru}(\text{CO})_3 \xrightarrow{L} \text{Ru}(\text{CO})_3 \\
\text{I} \quad \text{II} \quad \text{III} \\
3 \text{Ru}(\text{CO})_3 \end{array} \]  

(27)

An intermediate that can readily revert back to Ru₃(CO)₁₂, such as I or II, is clearly formed, since it has been shown that the quantum yield of photofragmentation in the presence of CO to give Ru(CO)₃₈

\[ \text{Ru}_{3}(\text{CO})_{12} + \text{CO} \xrightarrow{hv} 3 \text{Ru}(\text{CO})_3 \]  

(28)

is markedly dependent upon CO concentration and on the solvent employed (18). The [CO] dependence implies formation of an intermediate that can react with CO to give products or can relax back to the starting complex, with the quantum yield for product formation increasing as [CO] increases since the CO molecules more effectively compete for capture of the intermediate. The limiting quantum yield of reaction (26) under 1 atm CO pressure in isooctane solution is 0.065 (18).

Only a few clusters of nuclearity >3 have had their photochemistry examined (1, 19, 20), but the general result is that photoinduced fragmentation does not readily occur and instead photosubstitution chemistry dominates their photo-reactivity, although even photosubstitution occurs with quite low quantum yields (φ > 0.05), e.g., eqn. (29).

\[ \text{H}_2\text{FeRu}_{3}(\text{CO})_{12} + \text{PPh}_3 \xrightarrow{hv} \text{H}_2\text{FeRu}_{3}(\text{CO})_{12}(\text{PPh}_3) + \text{CO} \]  

(29)

**Concluding Remarks**

In general, it now appears that mononuclear carbonyls nearly always undergo photoinduced CO loss, dinuclear single metal-metal bonded carbonyls usually undergo metal-metal bond homolysis upon photolysis, and clusters with nuclearity >3 show low quantum yield photofragmentation chemistry. Trinuclear clusters are in the transition region, and examples of both photosubstitution and photofragmentation are known. Of course, a large number of other organometallic compounds have had their photochemical reactions examined, including olefin, alkyl, carbene, arene, hydride, and phosphine complexes, and a few general trends are beginning to emerge from these studies (1). However, space does not permit a detailed discussion of these other classes of organometallic compounds and the interested reader is referred to references (1) and (2).

Although the field of organometallic photochemistry is still relatively immature compared to the state of inorganic and organic photochemistry, a few guiding principles have begun to emerge. Certainly, photochemistry is a valuable synthetic technique and any practicing synthetic organometallic chemist should be familiar with the various photochemical methods for synthesis. There have been a few demonstrations of interesting photocatalytic chemistry, ranging from olefin isomerization, hydrogenation, hydrosilylation, and hydroformylation and this is a general area which needs further exploration. We also need more fundamental studies to define the basic photochemical reactions and the factors that affect the choice of photodecay pathways in organometallic compounds.

**Literature Cited**


