at the π-bond would be kinetically less favorable than the electron transfer in this particular substrate, which has an exceptionally low IP (IP_v = 7.5 eV).[19b] The combination of the resultant ion pairs yields **37**, which culminates in the production of **36**. The intermediacy of **37** was verified by conducting the reaction in either acetonitrile or acetone. The products obtained in the reactions in these solvents were **38** and **39**, respectively. Apparently, the dipolar addition of **37** to the heteromultiple bond in the solvent molecules took place.[35c,43]

Dispiro[2.0.2.4]deca-4,6-diene[1d,44] undergoes cycloaddition with TCNE in dioxane to afford a benzocyclooctane derivative as the major adduct.[1d] Cleavages of the two cyclopropane rings take place. Since most other dienophiles produce the normal Diels–Alder adducts,[45] a mechanism similar to those discussed above has been proposed by de Meijere.[1d]

Concluding Remarks

In spite of the fact that the thermal cycloadditions of cyclopropanes with olefins can rarely be accomplished, **18** produced a variety of cycloadducts in its reactions with various unsaturated compounds. The ready rearrangement of the incipient 1,3-biradical **29** to the 1,8-biradical **30**, which may have a prolonged lifetime owing to the intervention of an aromatic ring between the two radical centers, as well as the repeated production of the biradical species under the reaction conditions, might be the reason for the successes.

Some heavily substituted cyclopropylethylenes, **1**, reacted with TCNE to afford vinylcyclopentane derivatives, **3**. Certain tetrasubstituted 1,2-dicyclopropylethylenes **31**, reacted with TCNQ to afford [10]paracyclophadienes, **32**, and the dispiro compound **18** produced [3.3]paracyclophane, **36**, in its reaction with TCNQ. The success of these cycloadditions is ascribed to the low IP of the substrate ethylenes, the high EA of TCNE or TCNQ, and, in some cases, the difficulties for the access of TCNE or TCNQ to the π-bond in the reactants. Thus, an initial electron transfer is assumed, and the reactions of the resultant radical ion pairs appear to be accompanied by the efficient cyclopropane cleavage in the subsequent steps. In the paracyclophane formations with TCNQ, the intramolecular nucleophilic opening of the cyclopropane ring at the final stage of the reaction appears to be essential.[31]

The thermal ring-opening cycloadditions of cyclopropyl derivatives have not yet been well-explored, but some promising developments have been achieved as illustrated in this Account.

It is a great pleasure to acknowledge the contributions of our very able collaborators: Drs. T. Teraji, N. Shimizu, M. Murakami, T. Shibata, Y. Hienuki, and F. Kataoka and M. Ishikawa, K. Ishikura, S. Ishizuka, and T. Fujioka. The studies described here have been supported by a Grant-in-Aid for Scientific Research administered by the Ministry of Education, Science and Culture, and by the funds provided by Kuraray Co. Ltd. and the Kurata Foundation, to whom we are grateful.

(44) de Meijere, *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 899.

(45) de Meijere, A. *Chem. Ber.* **1974**, *107*, 1702. Kaufmann, D.; de Meijere, A.; Hingerty, B.; Saenger, W. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 816. Kaufmann, D.; de Meijere, A. *Tetrahedron Lett.* **1979**, 779.

Nonhomolytic Cleavage Pathways in the Photochemistry of Metal–Metal-Bonded Carbonyl Dimers

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The dominant photochemical process of many metal–metal-bonded carbonyl dimers is homolytic cleavage of the metal–metal bond to produce two 17-electron metal carbonyl fragments (eq 1).[1] The results of numerous photochemical, flash photolysis, and ESR spin-trapping experiments are consistent with this conclusion.[1]

$$L_nM\text{–}ML_n \xrightarrow{h\nu} L_nM + ML_n \tag{1}$$

For a considerable period of time it was thought that all of the photochemistry of metal–metal-bonded carbonyl complexes could be explained by invoking the primary photoprocess in eq 1. Recent results, however, suggest that other primary photoprocesses might also be important in accounting for the photochemistry of these complexes. It is noteworthy that the mechanistic evidence for primary photoprocesses other than homolytic cleavage is often less than definitive. From our examination of these reactions, we hope to draw some conclusions about the relative importance of nonhomolytic cleavage pathways in the photochemistry of metal–metal-bonded carbonyl dimers.

Electronic Excited States of Metal–Metal-Bonded Complexes

Of the molecules discussed in this account, detailed electronic spectral studies have been carried out only

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(1) The most recent review dealing with the photochemistry of metal carbonyl dimers can be found in Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979.

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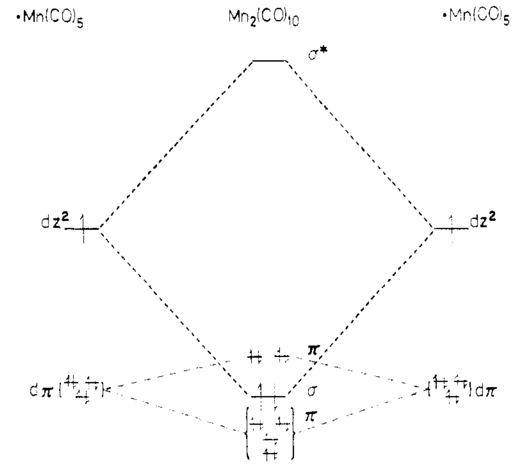
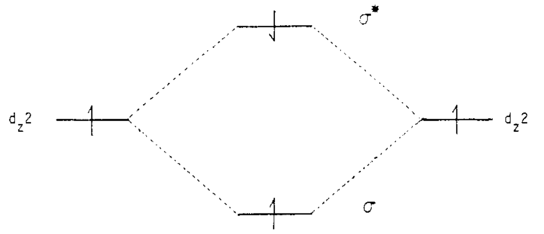


Figure 1. Molecular orbital scheme for the $Mn_2(CO)_{10}$ complex.[2] Only the orbitals involved in metal–metal bonding are shown.

on the $M_2(CO)_{10}$ (M = Mn, Re) complexes.[2] Levenson and Gray[2] performed an extended Hückel MO calculation on the $Mn_2(CO)_{10}$ complex (Figure 1) and showed that the two lowest energy excited states in those complexes were a dπ → σ* and the σ → σ* transitions. The electronic spectra of the other metal carbonyl dimers are similar to those of the $M_2(CO)_{10}$ complexes, and for this reason, the lowest energy bands in the other metal carbonyl dimers are generally assumed to be dπ → σ* and σ → σ* transitions. It is important to point out, however, that the band assignments for the other complexes are not based on rigorous spectroscopic investigations. In fact, Caspar and Meyer[3] have pointed out that these assignments are probably not correct for complexes with bridging CO ligands or with cyclopentadienyl ligands.

What kind of photochemistry is predicted as a result of excitation to the dπσ* and σσ* excited states? Consider the σ → σ* transition. On the basis of one-electron molecular orbital diagrams, the argument is usually made that no net metal–metal bonding exists in this excited state:



Therefore, the metal–metal bond breaks. (Why it should cleave homolytically is not explained.) This interpretation is quite simplified and can lead to incorrect predictions. A better understanding of the photochemistry can be had if we consider the potential energy surfaces arising from the σ^2, $\sigma\sigma^*$ (triplet), and $\sigma\sigma^*$ (singlet) electronic configurations. The bonding of two 17-electron ML_n species is analogous to the bonding of two H atoms so we can base our diagrams on those for the H_2 molecule.[4] As shown in Figure 2, the triplet state correlates at infinite separation with two 17-electron species and the excited singlet state correlates with the anion and cation. Thus, heterolytic cleavage can result from excitation to the singlet σσ* state and homolytic cleavage results from the triplet σσ* state.[5] In order for heterolytic cleavage to occur, the molecule must be excited to a level above the dissociation limit of the σσ* singlet state. Obviously, if the dissociation limit can be lowered in energy, then heterolytic cleavage becomes energetically more reasonable. The important points to learn from discussion are (1) that heterolytic cleavage of the metal–metal bond is possible and (2) that homolytic cleavage occurs from the excited triplet state.[5] These two features of metal–metal-bond photochemistry have not generally been recognized.

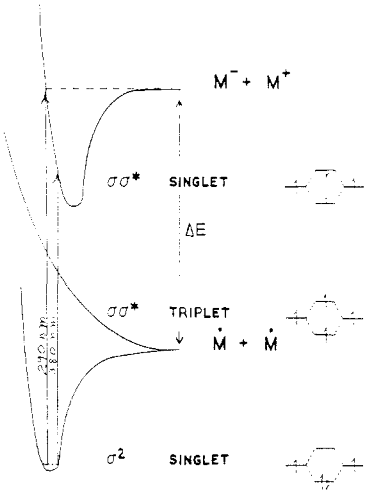


Figure 2. Proposed relationship of the potential energy surfaces for the σ^2, $\sigma\sigma^*$ (triplet), and $\sigma\sigma^*$ (singlet) states of metal–metal-bonded complexes. The σ^2 and $\sigma\sigma^*$ (triplet) states correlate to two 17-electron fragments at infinite separation of the metals. The $\sigma\sigma^*$ (singlet) state correlates to ionic species at infinite separation.

In several instances, metal carbonyl dimers have been irradiated in the ultraviolet at wavelengths higher in energy than the dπ → σ* or σ → σ* bands.[6] Gray and Levenson's work suggests that the transitions in this spectral region are M → CO(π*) charge-transfer transitions.[2] The π* orbitals are M–C antibonding so M–CO bond dissociation should result from excitation to these excited states if internal conversion to the lower energy excited states is not exceptionally fast.

M–CO Bond Dissociation Pathways

The primary photoprocess of mononuclear metal carbonyl complexes is M–CO bond dissociation.[7] It is logical to expect, therefore, that M–CO bond dissociation might also result from excitation of metal–metal-bonded carbonyl dimers. In fact, photochemical M–CO bond dissociation has been claimed for four metal carbonyl dimers: $Cp_2Mo_2(CO)_6$[8] (Cp = η^5-C_5H_5), $Mn_2(CO)_{10}$,[9] $Co_2(CO)_8$,[6] and $Cp_2Fe_2(CO)_4$.[3]

In the case of the $Cp_2Mo_2(CO)_6$ complex, Hughey et al.[8] observed an intermediate species believed to be $Cp_2Mo_2(CO)_5$ when they flash photolyzed $Cp_2Mo_2(CO)_6$

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(2) Levenson, R. A.; Gray, H. B. *J. Am. Chem. Soc.* **1975**, *97*, 6042–6047.

(3) Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 7794–7795.

(4) Coulson, C. A.; Fischer, I. *Philos. Mag.* **1949**, *40*, 386–393.

(5) Of course, other excited states between the σσ* singlet and triplet states may also lead to homolytic cleavage.

(6) Sweany, R. L.; Brown, T. L. *Inorg. Chem.* **1977**, *16*, 421–424.

(7) Wrighton, M. S. *Chem. Rev.* **1974**, *74*, 401–429.

(8) Hughey, J. L., IV; Bock, C. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1975**, *97*, 4440–4441.

(9) Rothberg, L. J.; Copper, N. J.; Peters, K. S.; Vaida, V. *J. Am. Chem. Soc.* **1982**, *104*, 3536–3537.

in cyclohexane, THF, or acetonitrile solution. The metal-metal bond homolysis product, $CpMo(CO)_3$, was also formed in the flash experiments. Evidence for the formation of the $Cp_2Mo_2(CO)_5$ species consisted of the following observations. (1) The intermediate reacted thermally to regenerate the starting material, $Cp_2Mo_2(CO)_6$. The second-order rate constants (20 ± 2 °C) for the decay of the intermediate were estimated as follows: 3×10^7 (acetonitrile), 5×10^7 (THF), and $1 \times 10^8\ M^{-1}\ s^{-1}$ (cyclohexane). Similar rate constants have been reported for the reaction of coordinatively unsaturated mononuclear metal carbonyl complexes with CO so the decay of the intermediate was proposed to involve recombination with CO (eq 2). (2) The electronic absorption spectrum of the intermediate exhibited an intense band in the near-UV region; the band was close in energy to the $\sigma \rightarrow \sigma^*$ band of the starting complex. This band was assigned to the $\sigma \rightarrow \sigma^*$ absorption of the intermediate, indicating the presence of a metal-metal bond in the intermediate.

$$Cp_2Mo_2(CO)_5 + CO \rightarrow Cp_2Mo_2(CO)_6 \qquad (2)$$

Although $Cp_2Mo_2(CO)_5$ appears to form by the flash photolysis of $Cp_2Mo_2(CO)_6$, Hughey, Bock, and Meyer were quite careful to point out that there is no clear evidence that M-CO bond dissociation is a primary photoprocess.[10] This latter point is an acute observation because Brown and co-workers would later show that $Mn_2(CO)_9$ can arise from secondary thermal reactions occurring after the initial homolysis of the Mn-Mn bond in $Mn_2(CO)_{10}$.[14] Thus, there is no definitive evidence that any *net* photochemical reactions of $Cp_2Mo_2(CO)_6$ result from an initial Mo-CO bond dissociation process.[10]

$Mn_2(CO)_{10}$ is the prototypical molecule that undergoes homolytic cleavage of the metal-metal bond upon irradiation. Much effort has recently been expended on determining if other photoprocesses occur upon excitation of this molecule. Wegman et al. have reported the results of a flash photolysis study of $Mn_2(CO)_{10}$ (microsecond time scale).[14] The major conclusion of their work is that metal-metal bond homolysis is the only important primary photoprocess in the $Mn_2(CO)_{10}$ complex. Transient absorption peaks attributed to $Mn_2(CO)_9$ and $Mn_2(CO)_8$ were observed, but the observation that the maximum concentration of these species is reached only after 60 ms or longer—a period too long after the flash to attribute the intermediate to a primary photoproduct—is evidence against formation of these species by Mn-CO bond dissociation. The following pathway was proposed to account for the formation of $Mn_2(CO)_9$ and $Mn_2(CO)_8$:

$$Mn_2(CO)_{10} \xrightarrow{h\nu} 2Mn(CO)_5 \qquad (3)$$

$$Mn(CO)_5 \rightarrow Mn(CO)_4 + CO \qquad (4)$$

$$Mn(CO)_4 + Mn(CO)_5 \rightarrow Mn_2(CO)_9 \qquad (5)$$

$$Mn(CO)_4 + Mn(CO)_4 \rightarrow Mn_2(CO)_8 \qquad (6)$$

$$Mn_2(CO)_8 + CO \rightarrow Mn_2(CO)_9 \qquad (7)$$

Results similar to those observed with $Mn_2(CO)_{10}$ were obtained with $Re_2(CO)_{10}$.

A more recent paper by Rothberg et al. also reports on the flash photolysis of $Mn_2(CO)_{10}$ and concludes that Mn-CO bond dissociation does occur upon irradiation of $Mn_2(CO)_{10}$.[9] In these experiments, a 25-ps excitation pulse was used (355 nm), and transient spectra were recorded between 0 and 250 ns after the pulse; ethanol was used as the solvent. No changes were observed in the spectra during the time 0–250 ns after the pulse. Spectra attributable to two different transients were observed; one spectrum was attributed to $Mn(CO)_5$ by comparison to the known spectra produced by pulse radiolysis and matrix isolation experiments. The other transient spectrum was suggested to be that of $Mn_2(CO)_9(EtOH)$, although the exact nature of the species was not determined. One thing is certain, however: the transient spectrum is not attributable to a secondary (thermal) product because it is formed within 25 ps of the flash—a period too short for secondary reactions of $Mn(CO)_5$ to occur. The transient must, therefore, be formed by a photoprocess other than Mn-Mn bond homolysis. Assignment of the transient absorption spectrum to $Mn_2(CO)_9(EtOH)$ was based on the similarity of its spectrum to that of $Mn_2(CO)_9(py)$ (λ_{max} 450 and 480 nm in $Mn_2(CO)_9(py)$ and the intermediate, respectively).[15]

As the discussion above indicates, the Brown-Faulkner and Peters-Vaida groups are in apparent disagreement as to the importance of Mn-CO bond dissociation in the $Mn_2(CO)_{10}$ molecule. Interestingly, very recent work by Wrighton and Hepp[17] suggests that excited $Mn_2(CO)_{10}$ molecules undergo Mn-CO bond dissociation as much as 30% of the time. Because the resulting $Mn_2(CO)_9$ intermediate can react with PPh_3 to form $Mn_2(CO)_9PPh_3$, Wrighton and Hepp concluded that Mn-CO bond dissociation is an important photochemical pathway in the $Mn_2(CO)_{10}$ complex.

In 1977, Sweany and Brown reported that irradiation (254 nm) of $Co_2(CO)_8$ at 12 K in argon matrices produced $Co_2(CO)_7$.[6] Evidence for the formation of $Co_2(CO)_7$ consisted of the following observations: (1) The infrared bands of the photolysis product could not be attributed to any of the mononuclear cobalt carbonyl species and (2) the photolysis product reacted with CO to regenerate $Co_2(CO)_8$. Interestingly, 254-nm radiation was required to produce $Co_2(CO)_7$ from $Co_2(CO)_8$; no changes were observed when the $Co_2(CO)_8$ was irradiated at 350 nm, as monitored by IR spectroscopy. Ir-

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[10] Hughey, Bock, and Meyer also pointed out that the known substitution reactions of $Cp_2Mo_2(CO)_6$ with phosphines and phosphites to form $Cp_2Mo_2(CO)_5L$ and $Cp_2Mo_2(CO)_4L_2$ are consistent with an M-CO bond dissociation primary photoprocess.[11,12] However, it has since been shown with other metal carbonyl dimers that substitution can occur via a pathway involving initial homolytic cleavage of the metal-metal bond.[13] A similar substitution pathway can probably account for some, perhaps all, of the substitution products in the case of the $Cp_2Mo_2(CO)_6$ complex.

[11] Haines, R. J.; Nyholm, R. S.; Stiddard, M. H. G. *J. Chem. Soc. A* **1966**, 1606–1607.

[12] Haines, R. J.; CuPreez, A. L.; Marais, I. L. *J. Organomet. Chem.* **1971**, *28*, 97–104.

[13] Kidd, D. R.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 4095–4103.

[14] Wegman, R. W.; Olsen, R. J.; Gard, D. R.; Faulkner, L. R.; Brown, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 6089–6092.

[15] For the sake of completeness, we point out that neither the Peters-Vaida group nor the Brown-Faulkner group was able to reproduce earlier observations of a very long-lived intermediate formed by the (repeated) flash photolysis of $Mn_2(CO)_{10}$ in cyclohexane.[16]

[16] Hughey, J. L., IV; Anderson, C. P.; Meyer, T. J. *J. Organomet. Chem.* **1977**, *125*, C49–C52.

[17] Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* in press.

radiation at 350 nm excites the $Co_2(CO)_8$ molecule in the $\sigma \rightarrow \sigma^*$ band[6] (λ_{max} for this transition is at 347 nm). The excited state at 254 nm leading to Co–CO bond dissociation is most likely a Co $\rightarrow$ CO(π^*) charge-transfer excited state. M–CO bond dissociation as a result of this type of excitation is expected.

The molecules we have discussed up to now are proposed to undergo M–CO bond dissociation from the same excited states that lead to M–M bond homolysis:

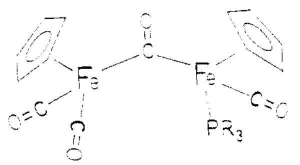
$$L_nM\text{-}ML_n \longrightarrow (L_nM\text{-}ML_n)^* \begin{array}{l} \longrightarrow 2ML_n \\ \longrightarrow L_nM\text{-}ML_{n-1} + L \end{array}$$

The $Co_2(CO)_8$ complex is quite different in this respect because there is no evidence that Co–CO bond dissociation occurs with low-energy $\sigma \rightarrow \sigma^*$ or $d_\pi \rightarrow \sigma^*$ excitation. Rather, CO dissociation appears to be the result of excitation to a higher energy excited state.

To conclude this discussion of $Co_2(CO)_8$, we point out that while there is good evidence that Co–CO bond dissociation occurs with 254-nm irradiation of $Co_2(CO)_8$, there is no evidence that photolytic Co–CO bond dissociation leads to any *net* reactivity of $Co_2(CO)_8$. $Co_2(CO)_7$ has been implicated in the thermal reactions of $Co_2(CO)_8$, however.[18] One final note regarding $Co_2(CO)_8$: Brown and Sweany showed that $Co_2(CO)_8$ exists in three isomeric forms.[19] The relationship between the structures of $Co_2(CO)_8$ and the primary photoprocess has not been determined.

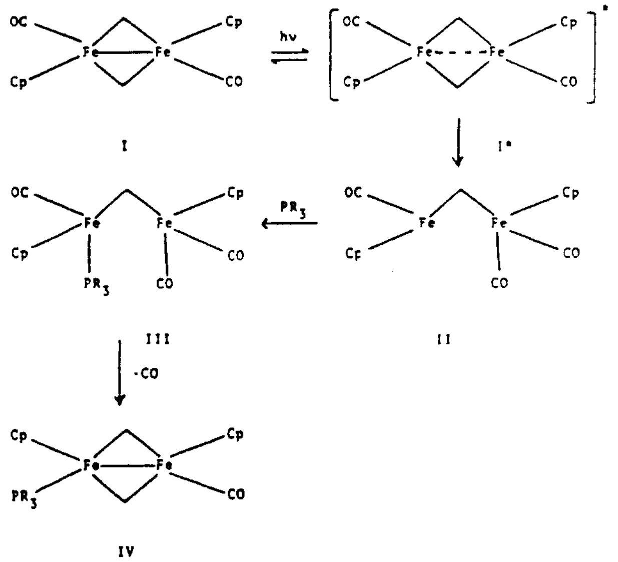
Isomer Formation

Isomerization of the ground-state structure is suggested to be the primary photoprocess for several metal–metal-bonded carbonyl dimers. The most definitive evidence for a process of this type comes in the case of the $Cp_2Fe_2(CO)_4$ complex.[20] As part of their study of the photosubstitution reactions of this complex, Tyler et al.[20] irradiated the complex at −78 °C in ethyl chloride and THF solutions. Under these conditions, in the presence of phosphines or phosphites, a yellow reaction intermediate formed and was spectroscopically characterized. The structure below was proposed for the intermediate:



On warming of the cold solution containing the yellow intermediate to room temperature, the yellow species disappears and the green product $Cp_2Fe_2(CO)_3(PR_3)$ forms.

On the basis of their observation of this intermediate and on a Stern–Volmer relationship for the reaction of $Cp_2Fe_2(CO)_4$ with PPh_3 at room temperature, Tyler et al. proposed that $Cp_2Fe_2(CO)_4$ reacted with phosphines and phosphites according to the following scheme:[20]



The important point, of course, is that it was not necessary to postulate Fe–Fe bond homolysis as the primary photoprocess leading to the formation of $Cp_2Fe_2(CO)_3(PR_3)$. The authors attributed the formation of the intermediate I* to the presence of bridging CO groups which prevented the two halves of the molecule from separating when the Fe–Fe bond was weakened by $\sigma \rightarrow \sigma^*$ or $d\pi \rightarrow \sigma^*$ excitation. In addition to being involved in the substitution reactions of $Cp_2Fe_2(CO)_4$, Tyler et al.[20] suggested that intermediate II might also be involved in the reactions of $Cp_2Fe_2(CO)_4$ with halocarbons to produce monomeric species of the type $CpFe(CO)_2X$.[21] The basis for this suggestion was the observation that the yellow intermediate (III) reacted with CCl_4 in the dark to give only $CpFe(CO)_2Cl$.

A flash-photolysis study by Caspar and Meyer[3] substantiates the claim by Tyler et al.[20] that Fe–Fe bond homolysis is not involved in the photochemical substitution reactions of the $Cp_2Fe_2(CO)_4$ complex with certain phosphines and phosphites. Caspar and Meyer observed two intermediates (one was long-lived, the other short-lived) following the flash photolysis ($\lambda > 250$ nm or $\lambda > 400$ nm) of $Cp_2Fe_2(CO)_4$ in cyclohexane or benzene solutions. The short-lived intermediate decayed by second-order kinetics to re-form the dimer and was consequently suggested to be the $CpFe(CO)_2$ species. The longer lived intermediate decayed to the dimer by first-order kinetics, reacted with PPh_3 to give $Cp_2Fe_2(CO)_3(PPh_3)$, and was consequently suggested to be $Cp_2Fe_2(CO)_3$. Although Caspar and Meyer believed their long-lived intermediate to be $Cp_2Fe_2(CO)_3$, Tyler and Gray[22] pointed out that the spectroscopic data are consistent with this being intermediate II in their scheme (i.e., the long-lived intermediate is a non-metal–metal-bonded, CO-bridged species). Despite the difference in the Gray and Meyer structural assignments for the intermediate, the important point is that $Cp_2Fe_2(CO)_4$ provides the first definitive example of a metal–metal-bonded carbonyl dimer that does net photochemistry by reacting via a non-metal–metal bond homolysis pathway.[23]

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[18] Brown mentions several examples in ref 6. See ref 6–8 of his paper.

[19] Sweany, R. L.; Brown, T. L. *Inorg. Chem.* **1977**, *16*, 415–421.

[20] Tyler, D. R.; Schmidt, M. A.; Gray, H. B. *J. Am. Chem. Soc.* **1979**, *101*, 2753–2755.

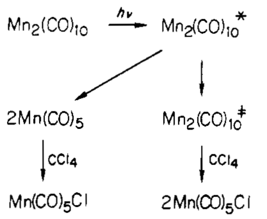
[21] Giannotti, C.; Merle, G. *J. Organomet. Chem.* **1976**, *105*, 97–100.

[22] Tyler, D. R.; Schmidt, M. A.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 6018–6021.

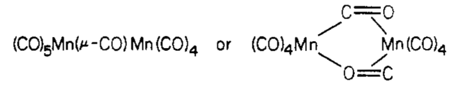
The only other system in which an isomer of the ground-state structure has been implicated as an intermediate is the photoreaction of $\mathrm{Mn_2(CO)_{10}}$ with $\mathrm{CCl_4}$. Poë and Fox studied the quantum yields of reaction 8 as a function of radiation intensity.[26] Their analysis

$$\mathrm{Mn_2(CO)_{10}} \xrightarrow[\mathrm{CCl_4}]{h\nu} 2\mathrm{Mn(CO)_5Cl} \tag{8}$$

led them to conclude that $\mathrm{Mn(CO)_5Cl}$ was formed by two independent pathways. One pathway is the usual



pathway involving homolytic cleavage of the Mn–Mn bond, and the other pathway involves the formation of an isomeric form of $\mathrm{Mn_2(CO)_{10}}$, labeled as $\mathrm{Mn_2(CO)_{10}}^{\ddagger}$ in the scheme. The structure of $\mathrm{Mn_2(CO)_{10}}^{\ddagger}$ was not investigated, but the following two structures were suggested:



It would be constructive to reinterpret the Poë–Fox quantum yield results in terms of the Wrighton–Hepp,[17] Brown–Faulkner,[14] and Peters–Vaida[9] results (i.e., $\mathrm{Mn_2(CO)_{10}}^{\ddagger}$ might be $\mathrm{Mn_2(CO)_9}$).

Photochemically Induced Heterolytic Cleavage

The primary photoprocess in certain disproportionation reactions of metal carbonyl dimers is proposed to be heterolytic cleavage of the metal–metal bond. For example, Allen, et al.[27] reported that irradiation of $\mathrm{M_2(CO)_{10}}$ (M = Mn, Re) in pyridine, $\mathrm{Me_2SO}$, DMF, dioxane, or cumene gives the product $\mathrm{[M(solvent)_6][M(CO)_5]_2}$. The origin of the $\mathrm{M(solvent)_6}^{2+}$ product in these reactions was not explained by Allen, et al., but later work by McCullen and Brown[28] showed that the M(II) species probably forms from $\mathrm{Mn(CO)_3(solvent)_3}^+$ (the expected Mn(I) product) by the following reaction:

$$3\mathrm{Mn(CO)_3(solvent)_3}^+ + 3\,\mathrm{solvent} \xrightarrow{h\nu} 2\mathrm{Mn(solvent)_6}^{2+} + \mathrm{Mn(CO)_5}^- + 4\mathrm{CO} \tag{9}$$

Two possible disproportionation mechanisms were discussed by the authors.[27] One proposed mechanism involved the initial direct heterolytic cleavage of the metal–metal bond (eq 10). The other proposed

$$\mathrm{M_2(CO)_{10}} \xrightarrow{h\nu} \mathrm{M(CO)_5}^+ + \mathrm{M(CO)_5}^- \tag{10}$$

mechanism involved M–M bond homolysis followed by electron transfer (eq 11 and 12). No detailed mechanistic work was done to distinguish between the two

$$\mathrm{L}_n\mathrm{M{-}ML}_n \xrightarrow{h\nu} \mathrm{ML}_n + \mathrm{ML}_n \tag{11}$$

$$\mathrm{ML}_n + \mathrm{ML}_n \rightarrow \mathrm{ML}_n^{\ +} + \mathrm{ML}_n^{\ -} \tag{12}$$

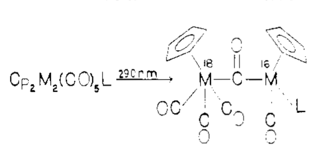
proposed mechanisms, but it was suggested that quantum yield data supported the heterolytic rather than the homolytic mechanism.

Subsequent work by McCullen and Brown[28] on the disproportionation reaction of $\mathrm{Mn_2(CO)_{10}}$ in pyridine showed that the reaction followed a radical-chain mechanism and was initiated by photochemical homolytic cleavage of the Mn–Mn bond. The same mechanism is also likely in the other solvents used by Allen et al.

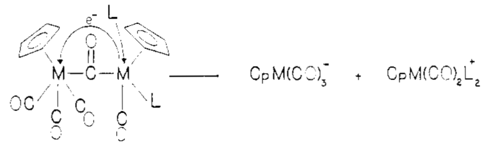
Later work by Stiegman and Tyler[29] showed that a related but not identical radical-chain mechanism was also operable in the disproportionation reactions of the $\mathrm{Cp_2M_2(CO)_6}$ complexes in the presence of small phosphines and phosphites (eq 13). For the larger phos-

$$\mathrm{Cp_2Mo_2(CO)_6} + 2\mathrm{PR_3} \rightarrow \mathrm{CpMo(CO)_2(PR_3)_2}^+ + \mathrm{CpMo(CO)_3}^- + \mathrm{CO} \tag{13}$$

phines (e.g., $\mathrm{PPh_3}$), however, a different pathway is followed.[30] For the larger phosphines, Stiegman and Tyler showed that irradiation into the $\sigma \rightarrow \sigma^*$ (390 nm) or the $d\pi \rightarrow \sigma^*$ (505 nm) bands of the $\mathrm{Cp_2M_2(CO)_6}$ complexes did not lead to the disproportionation in eq 13. Apparently, a higher energy excited state is involved because disproportionation did not occur until the excitation wavelength was about 290 nm or shorter. Since it is well-established that homolytic cleavage of the Mo–Mo bond occurs with either 366- or 504-nm excitation, Stiegman and Tyler concluded that homolytic cleavage of the Mo–Mo bond was not sufficient to initiate or cause disproportionation of the $\mathrm{Cp_2Mo_2(CO)_6}$ complex. The disproportionation pathway utilized in the presence of larger phosphines was not determined, but a pathway involving the formation of a CO-bridged non-metal–metal-bonded intermediate was suggested:



I



The problem with this mechanism is that intermediate I is certainly lower in energy than two 17-electron $\mathrm{CpM(CO)_3}$ fragments; it is not obvious why a higher energy excitation leads to a lower energy intermediate.

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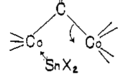
[23] We note that CO-bridged intermediates similar to the one proposed by Tyler et al.[20] have been proposed in numerous thermal reactions of metal–metal-bonded dimers.[24] In addition, a CO-bridged species was proposed as an intermediate in the photochemical insertion reaction of $\mathrm{SnCl_2}$ with $\mathrm{Co_2(CO)_6(PR_3)_2}$, yielding $\mathrm{(PR_3)(CO)_3Co{-}SnCl_2{-}Co(CO)_3(PR_3)}$.[25] Kinetic evidence was consistent with the formation of the intermediate below



but a pathway involving geminate radical pairs could not be ruled out.

[24] Barrett, P. F.; Sun, K. K. W. *Can. J. Chem.* **1970**, *48*, 3300–3303. This work was latter questioned. See: Cotton, J. D.; Trewin, A. *J. Organomet. Chem.* **1976**, *117*, C7–C9.

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[30] Stiegman, A. E.; Tyler, D. R. *J. Am. Chem. Soc.* **1982**, *104*, 2944–2945.

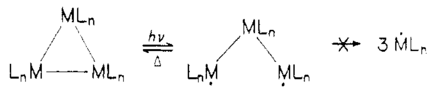
Alternative mechanisms involving initial M–CO bond dissociation or direct heterolytic cleavage are possible. Inspection of Figure 2 shows that heterolytic cleavage of a metal–metal-bonded complex may result if the complex is excited above the dissociation limit of the $\sigma\sigma^*$ (singlet) state. It can be argued that in the case of the $Cp_2M_2(CO)_6$ complexes, PPh_3 and other large phosphines are unable to react via the radical-chain pathway because of steric reasons, and therefore, the disproportionation occurs via direct heterolysis. The wavelength dependence of the reaction arises because 366-nm excitation is not sufficient to excite the complexes above the dissociation limit, whereas 290 nm will excite the complexes above the dissociation limit. There is no proof for this explanation and so all that can be said with certainty concerning the disproportionation of $Cp_2Mo_2(CO)_6$ with PPh_3 and other large phosphines is that the reactions do not proceed via homolytic cleavage of the metal–metal bond.

Conclusion

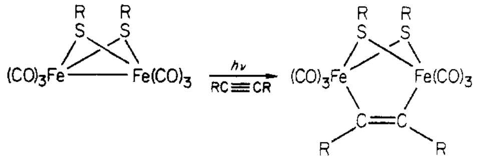
There is evidence that nonhomolytic cleavage processes result from the low-energy excitation of metal carbonyl dimers. However, with the exception of the phosphine and phosphite substitution reactions of $Cp_2Fe_2(CO)_4$ and $Mn_2(CO)_{10}$, it has yet to be definitely shown that these processes lead to net photochemical reactions. Clearly, homolytic cleavage of the metal–metal bond is the dominant process that leads to net reactivity at low energy.

When metal–metal-bonded dimers are irradiated at higher energy, it is not clear that homolytic metal–metal bond cleavage is so overwhelmingly important compared to other processes. Although the higher energy (UV irradiation) photochemistry of metal carbonyl dimers has not been systematically studied, preliminary studies suggest that nonhomolytic cleavage pathways are more important in describing the chemistry of the higher energy excited states.

Finally, we note that the metal carbonyl dimers may be the only class of metal cluster complexes that undergo facile fragmentation when irradiated. A current theme in the photochemical literature is that larger clusters do not fragment (even though the excited state is of a $\sigma \rightarrow \sigma^*$ type) because bridging groups or the remaining metal–metal bonds inhibit complete fragmentation:[31-34]



In the reaction above, the reverse reaction is facilitated by the presence of the "bridging" M–M bonds so the photochemistry must occur via another pathway, usually M–CO bond dissociation. Bridging ligands can also affect the chemistry of dimeric complexes. Examples of bridging ligands preventing fragmentation in metal carbonyl dimers are the phosphine substitution reactions of $Cp_2Fe_2(CO)_4$ discussed earlier and the insertion given in eq 14.[35] As photochemists move away from the simpler nonbridged metal carbonyl dimers to more complex bridged species, pathways other than homolytic cleavage will undoubtedly become increasingly important.[36]



(14)

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