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# Mechanisms and intermediates in the photochemistry of $M_2(CO)_6(\eta^5\text{-}C_5H_5)_2$, where $M = Cr$, Mo and W, and their ring-coupled analogs

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Dedicated to Professor Arthur Adamson in honor of his 80th birthday and a lifetime of fundamental contributions to the understanding of the photochemistry of metal compounds

## Contents

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## Abstract

The structure, bonding, and photochemistry of the Group VI cyclopentadienyl metal carbonyl compounds of the general form $(\eta^5\text{-}C_5H_5)_2M_2(CO)_6$, where M = Cr, Mo, and W, and their ring-substituted and ring-coupled derivatives is critically reviewed. The emphasis of this review is to bring together evidence for reaction intermediates and mechanisms to assist in the interpretation of the chemistry of these materials and to guide future investigations.

*Keywords:* Group VI compounds; Cyclopentadienyl carbonyl compounds; Photochemistry

## 1. Introduction

The photochemistry of $M_2(CO)_6(\eta^5\text{-}C_5H_5)_2$, where M = Cr (**1**), Mo (**2**) and W (**3**), has been the subject of investigation for 30 years during which time a number of techniques have been brought to bear on the question of the mechanism of these reactions and the fate of the several intermediates. Since the last review of this photochemical literature by Meyer and Caspar [1] in 1985, and the literature on 19-electron intermediates by Tyler in 1991 [2], important new results utilizing frozen matrices and time-resolved flash photochemical techniques have firmly established the identities of some of the photointermediates and allowed a culling of some proposed mechanisms. Further, the chemistry of the radical intermediates continues to be examined and evidence for 19 (or $18+\delta$) electron species has been strengthened. Although the mechanistic questions are still not completely resolved, the occasion of Professor Adamson's 80th birthday marks an appropriate time to review the current literature and to suggest avenues of investigation that may prove fruitful in the future.

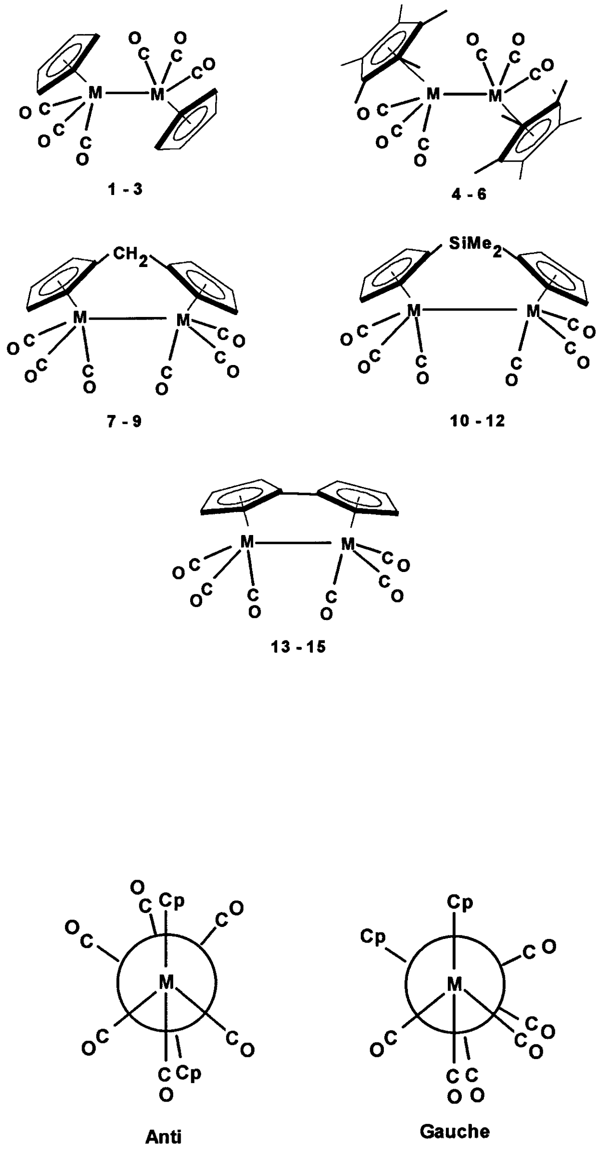
## 2. Structure and bonding

A rich synthetic chemistry of the Group VI cyclopentadienyl carbonyl bimetallic compounds has been developed since the first report of these compounds by

Table 1
M–M bond lengths (Å) for representative Group VI compounds

| Compound class | Cr–Cr | Mo–Mo | W–W |
|---|---|---|---|
| $M_2(CO)_6(\eta^5\text{-}C_5H_5)_2$ — *anti* | 3.281(1) [4] | 3.235(1) [5,6] | 3.222(1) [6] |
| — *gauche* | | 3.2239(11) [7] | |
| $M_2(CO)_6(\eta^5\text{-}C_5Me_5)_2$ | 3.3107(7) [8] | 3.278(14) $P2_1/c$ [9]<br>3.281(1) $P2_1/n$ [10] | 3.288(1) [11] |
| $M_2(CO)_6(\eta^5,\eta^5\text{-}C_5H_4\text{–}CH_2\text{–}C_5H_4)$ | 3.211(2) [12] | 3.1406 [13] | 3.166(1) [14] |
| $M_2(CO)_6(\eta^5,\eta^5\text{-}C_5H_4\text{–}SiMe_2\text{–}C_5H_4)$ | – | – | 3.196(1) [15] |
| $M_2(CO)_6(\eta^5,\eta^5\text{-}C_5H_4\text{–}C_5H_4)$ | 3.471 [16] | 3.371 [17] | 3.347(1) [17] |

Wilkinson in 1954 [3]. Derivatives include cyclopentadienyl, **1**–**3**, and pentamethylcyclopentadienyl, **4**–**6**, and a number of ring-coupled derivatives including those of bis(cyclopentadienyl)methane, **7**–**9**, bis(cyclopentadienyl)dimethylsilane, **10**–**12**, and fulvalene, **13**–**15**. Other derivatives will be introduced in the text.



**1 - 3**

**4 - 6**

**7 - 9**

**10 - 12**

**13 - 15**

**Anti**

**Gauche**

Fig. 1.

This review will focus on the photochemistry of these compounds and on the thermochemistry of the chromium compounds where the reactions of the resultant chromium radicals parallel those of photochemical bond homolysis products of molybdenum and tungsten.

The molecular structures of a number of compounds in this series have been reported and the M–M bond lengths are reported in Table 1.

Several trends are readily apparent from this data. Substitution of a $C_5Me_5$ ring for $C_5H_5$ lengthens the M–M bond, probably due to steric repulsions. Single atom coupling of rings results in a compression of the M–M bond relative to the cyclopentadienyl compounds, while the less flexible fulvalene rings result in lengthening of the bonds. Perhaps the most striking feature to arise from these structures is the unusually long Cr–Cr bond relative to those of the molybdenum and tungsten compounds. The Cr–Cr bond length for **1** is 0.06 Å *longer* than the Mo–Mo bond length of **2**. On the basis of related compounds, it has been estimated that the Cr–Cr bond length should be 0.38 Å *shorter* than the Mo–Mo bond [4]. The length of the Cr–Cr bonds is generally interpreted to parallel the overall weakness of these bonds as reflected by their physical and chemical properties to be described below.

Generally cyclopentadienyl derivatives are found to assume the more thermodynamically favorable *anti* conformation, Fig. 1, although the structure of the *gauche* rotamer of **2** has been reported [7]. Ring coupling restrains the molecular geometry such that compounds with single atom carbon or silane bridge tend to have *gauche* conformations, while the fulvalene compounds have fully eclipsed conformations of the metal carbonyls.

**1**–**3** exist in solution [6,18] in both the *anti* and *gauche* rotameric forms with a strong preference for the *anti* form. Indeed, in hydrocarbons at room temperature (r.t.) the *gauche* form of **2** is effectively absent. The energies of activation for the *anti* to *gauche* rotation have been estimated to be (**1**) $13.7 \pm 5$, (**2**) $15.3 \pm 3$ and (**3**) $15.2 \pm 4$ kcal $mol^{-1}$. Heats of hydrogenation of the M–M bonds in **1**–**3** have been determined and found to be (**1**) $-3.3$, (**2**) $+6.3$, and (**3**) $-1.5$ kcal $mol^{-1}$. It is generally found that M–H bond strengths increase on descending a triad. The anomalous behavior of **1** is attributed to an unusually weak Cr–Cr bond [19].

## 3. Thermal bond homolysis

Solution studies have established that **1** is in equilibrium with its bond homolysis radical $Cr(CO)_3(\eta^5\text{-}C_5H_5)$, Eq. (1), L = CO. The position of the dimer–radical equilibrium is sensitive to substituents on the ring and metal, thus for the series of compounds $Cr_2(CO)_6(\eta^5\text{-}C_5H_5)_2$, $Cr_2(CO)_6(\eta^5\text{-}C_5Me_5)_2$, and $Cr_2(CO)_4[P(OMe)_3]_2(\eta^5\text{-}C_5H_5)_2$, the thermodynamic parameters for bond homolysis are $\Delta H = 14.7 \pm 0.3$ kcal $mol^{-1}$, $\Delta S = 35.1 \pm 0.9$ cal $mol^{-1}$ $K^{-1}$; $\Delta H = 13.1 \pm 0.3$ kcal $mol^{-1}$, $\Delta S = 40.4 \pm 1.3$ cal $mol^{-1}$ $K^{-1}$; and $\Delta H = 11.7 \pm 0.3$ kcal $mol^{-1}$, $\Delta S = 42.0 \pm 3.0$ cal $mol^{-1}$ $K^{-1}$ [8,20].

$$Cr_2(CO)_{6-2n}L_{2n}(\eta^5\text{-}C_5H_5)_2 \rightleftharpoons Cr(CO)_{3-n}L_n(\eta^5\text{-}C_5H_5) \qquad (1)$$

Table 2
Electronic spectra of $M_2(CO)_6(\eta^5\text{-}C_5H_5)_2$

| M (solvent) | Band maxima, nm ($\varepsilon$) | Band maxima, nm ($\varepsilon$) |
|---|---|---|
| Cr (isooctane) | 590 | 488 |
| Mo ($CCl_4$) | 515 (1860) | 389 (21 000) |
| W ($CCl_4$) | 493 (2450) | 362 (20 200) |

The molecular structure of $Cr_2(CO)_4[P(OMe)_3]_2(\eta^5\text{-}C_5H_5)_2$ has been reported and the Cr–Cr bond length was found to be 3.343(1) Å, 0.062 Å longer than that in **1**, consistent with bond weakening and a shift of the bimetallic/radical equilibrium to the right [21].

In some cases the equilibrium may be shifted completely to the right even in the solid state. The stable 17-electron species, $Cr(CO)_2(PMe_3)(\eta^5\text{-}C_5Me_5)$ and $Cr(CO)_2(PPh_3)(\eta^5\text{-}C_5H_5)$, may be isolated as crystalline solids, and the molecular structures of these species have been determined confirming their monomeric nature [22a]. ESR studies on $Cr(CO)_3(\eta^5\text{-}C_5H_5)$ doped in $Mn(CO)_3(\eta^5\text{-}C_5H_5)$ and $Cr(CO)_2(PPh_3)(\eta^5\text{-}C_5H_5)$ doped in $Mn(CO)_2(PPh_3)(\eta^5\text{-}C_5H_5)$ established that the singly occupied molecular orbitals are $d_{x^2-y^2}$ and $d_{xy}$, respectively [22b–d].

In contrast to the dimer–radical equilibrium of **1**, the ring-coupled chromium compounds **7** [7], the 2,2-propyl bridged analog of **7** [23], **10** [15], and even the fulvalene compound **13** [17] are found to be strictly diamagnetic in solution suggesting either a suppression of the Cr–Cr bond homolysis or a facile recombination of radicals facilitated by ring coupling (effectively an enhanced 'cage effect' brought about by coupling). This latter possibility has gained credence with recent work on substituted derivatives of **13**, $Cr_2(CO)_4L_2(\eta^5,\eta^5\text{-}C_5H_4\text{–}C_5H_4)$, where $L = PMe_2$ or $PMe_3$, for which spectral and chemical evidence suggest spontaneous thermal bond homolysis [24].

## 4. Spectroscopy and theoretical models

Two bands are observed in the UV–visible spectra of **1**–**3**, Table 2, with the weak band at lower energy being assigned to a $d\pi\text{–}\sigma^*$ transition while the stronger band at higher energy is assigned to a $\sigma\text{–}\sigma^*$ transition localized on the metal–metal bond [25]. No significant shift in band maxima is observed in a range of solvents. The positions of the band maxima are sensitive to ring coupling with the energy of the bands increasing in the order: **2** < **8** < **14** [14]. Band assignments were made by analogy to those of $M_2(CO)_{10}$, where M = Mn and Re [26].

A qualitative molecular orbital model has been proposed to account for the observed spectra, Fig. 2 [25b]. In light of the continuing interest in these compounds it is surprising that more modern theoretical methods have not been brought to bear on their bonding.

Luminescence studies of **2** and **3** in cyclohexane at r.t. reveal two emission peaks. The higher energy emission for **2** appears at about 440 nm and is assigned to fluorescence from a weak metal–cyclopentadienyl π* transition while the origin of the lower energy emission at about 570 nm is unknown [27]. A referee has noted that these luminescence studies have not been reproduced and the reported emission bands may be due to an impurity.

## 5. Matrix isolation studies

Matrix isolation is an ideal methodology for examining photochemical intermediates [28] and has been applied to the investigation of the Group VI compounds using a variety of matrix materials. One limitation of matrix studies in the current case is that any metal-based $M(CO)_3(\eta^5\text{-}C_5H_5)$ radicals formed by M–M homolysis would recombine in the rigid matrix cavity. A study of cage effects on $M_2(CO)_6(\eta^5\text{-}C_5H_4CH_3)_2$, where $M = Mo$ and W, for conventional solvents has established that cage efficiency factors for recombination versus cage escape are a function of solution viscosity and radical size and mass [29]. As a frozen matrix may be considered to be a highly viscous solution, radicals will only be observed in unique cases. For example, photolysis of $M(CO)_3H(\eta^5\text{-}C_5H_5)$, $M = Mo$ of W, in a solid CO matrix permits the $M(CO)_3(\eta^5\text{-}C_5H_5)$ radical to be observed because a hydrogen atom is transferred to CO to form the relatively stable HCO radical [30].

Compounds **2**, **3**, and **5** have been photolyzed in polyvinyl chloride films (12–77 K) [31] and frozen gas matrices (Ar, $CH_4$, and CO) at 12 K [32]. In addition, $Mo_2(CO)_6(\eta^5\text{-}C_5H_4C_4H_9)_2$ has been photolyzed in Nujol glass at ca. 77 K [33]. In all cases, photolysis into either the high or low energy bands of the electronic spectrum gave rise to a photoproduct, **16**, that exhibits characteristic bands in the

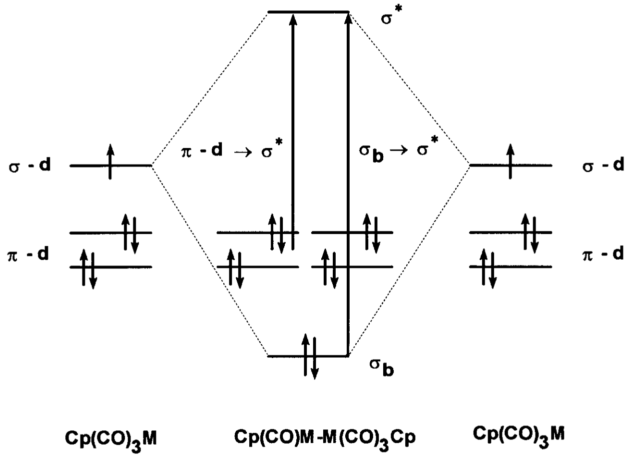
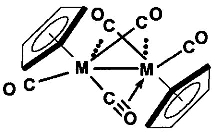
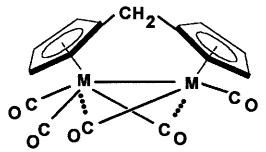


Fig. 2. MO diagram for assignment of electronic transitions of $M_2(CO)_6(\eta^5\text{-}C_5H_5)_2$ [25b].

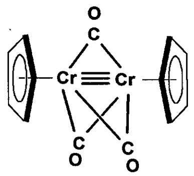
terminal, semibridging and four-electron bridging carbonyl regions. No photochemical 'back reaction' could be induced by photolysis of **16**, nor was $N_2$ incorporated as a ligand when the photolyses were carried out in frozen $N_2$ [32]. Complete reversal of the photoreaction in polyvinyl chloride films occurred when the films were warmed to 180 K [31].



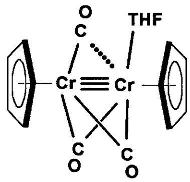
**16**



**19**



**17**



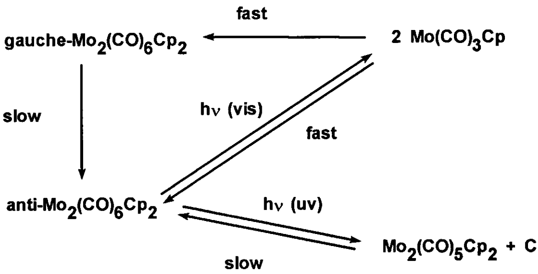
**18**

Photolysis of **2** and **3** in polyvinyl chloride films at r.t. resulted in the formation of $M_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ and $M(CO_3)(\eta^5\text{-}C_5H_5)Cl$ [31].

Photolysis of **2** and **3** in methyltetrahydrofuran glass at ca. 80 K has been reported to give rise to new IR bands attributed to $M(CO)_3(\eta^5\text{-}C_5H_5)$ radicals [34]. Reanalysis of the IR bands in the light of more recent work indicates that the species observed in methyltetrahydrofuran are more likely those of the CO-loss products, **16**.

Photolysis of **1** in polyvinyl chloride films did not result in the formation of any stable photoproducts although Cr–Cr bond homolysis is certainly taking place [31]. This result suggests that Cr–Cr bond homolysis is so facile that the CO-loss pathway for this compound is completely bypassed. Ring-coupled derivatives have not yet been examined in matrices and it will be interesting to establish whether CO-loss products are observed with these compounds. Photolysis of $Cr_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ in polyvinyl chloride films resulted in CO-loss and formation of a new species proposed to be the triply bridged dimer, **17**. Upon warming in polyvinyl chloride films cast from THF a new species was found to form that was proposed to be the THF complex, **18** [31]. Gas matrix studies could not be carried out on **I** because of decomposition during sublimation [32].

Photolysis into the high energy electronic transition of the ring-coupled compounds **8** and **9** in frozen Ar, $CH_4$ and CO matrices at 12 K gave rise to a CO-loss product, **19**, characterized by carbonyl stretching bands in the terminal and semi-bridging carbonyl regions. No products were found to result upon photolysis into the low energy bands of **8** and **9** [32]. The fulvalene compounds have not yet been examined in frozen matrices.



Scheme 1. Photochemical pathways for $Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2$ [36].

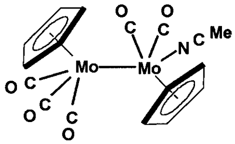
## 6. Time-resolved solution studies

Flash photolysis studies on **1**–**3** have been carried out by several groups. Early work using UV–visible detection [25c,35] established two distinct pathways for regrowth of **2** after photolysis with the slow pathway being ~ 50–100 times slower than the rapid pathway. The rapid pathway was attributed to $Mo(CO)_3(\eta^5\text{-}C_5H_5)_2$ radical recombination while the slow pathway was assumed to involve CO capture by a pentacarbonyl intermediate.

Recent studies employing time-resolved IR techniques have permitted exact identification of the various species, including the radicals, in solution and have resulted in a reinterpretation of the photochemistry [36,37]. The current state of the understanding of the photolysis of **2** is presented in Scheme 1.

Flash photolysis of **2** in 3-methylpentane at 200 K ($\lambda_{cutoff} = 450$ nm) or *n*-heptane at r.t. ($\lambda_{flash} = 532$ nm) results in formation of the radical, but no measurable CO-loss product, **13** (M = Mo). In *n*-heptane, the radical decays with second-order kinetics to form either *anti*- or *gauche*-**2**. The rate of radical recombination is calculated to be $3(\pm 1) \times 10^9$ $M^{-1}$ $s^{-1}$ [36].

The growth of *gauche*-**2** was monitored at 2020 $cm^{-1}$. There was an instantaneous formation of *gauche*-**2** following the flash, attributed to radical recombination within the solvent cage, followed by growth of *gauche*-**2** from out-of-cage radical recombination. *gauche*-**2** was found to relax to *anti*-**2** with a first order rate of 2.0 $(\pm 0.5) \times 10^2$ $s^{-1}$. This rate is effectively identical to the 'slow' process previously attributed to recapture of CO by a pentacarbonyl intermediate [36,37].



**20**

Photolysis in 3-methylpentane (200 K) at short wavelength was found to result in formation of both *gauche*-**2** and **16** (M = Mo). The ratio of these two species is 1:5

with short wavelength irradiation and 'at least' 6:1 with a cutoff filter ($\lambda_{\text{cutoff}} = 450$ nm). **16** (M = Mo) is surprisingly stable in solution at 200 K, but decays at 240 K with formation of **2** and $Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2$. Added CO shortens the lifetime of **16** (M = Mo) even at 200 K [36]. Flash photolysis of **2** at short wavelength was carried out in the presence of acetonitrile at 200, 248, 256, and 298 K. At 298 K only **2** and $Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ were observed 1 min after the flash. At lower temperatures, a species having five IR bands was observed that was assigned to the mono-substituted species, **20**. The apparent absence of doubly substituted products appears to rule out reaction of radical with acetonitrile to form $Mo(CO)_2(NCMe)(\eta^5\text{-}C_5H_5)$ that might dimerize to give $Mo_2(CO)_4(NCMe)_2(\eta^5\text{-}C_5H_5)_2$. It was noted that attempts to expand these studies to reactions of **16** with other ligands such as phosphines were precluded by disproportionation reactions [36].

The rate of $Cr(CO)_3(\eta^5\text{-}C_5R_5)$, R = H and Me, radical recombination has been determined in acetonitrile at 298 K using a flash ($\lambda_{\text{irr}} = 532$ nm) concentration jump method [38a]. This experiment is significant in that it is the only example of solution photolysis of **I** of which we are aware. The rates of the forward reactions were found to be $1.2 \pm 0.1 \times 10^5$ (R = H) and $5.6 \pm 0.5 \times 10^5$ $s^{-1}$ (R = Me) and the rates of the reverse reactions were found to be $2.7 \pm 0.2 \times 10^8$ (R = H) and $7.0 \pm 0.6 \times 10^6$ $M^{-1}$ $s^{-1}$ (R = Me). The rates of radical recombination for these compounds have also been measured using electrochemical techniques at 243 K in dichloromethane/0.1 M $NBu_4PF_6$ and found to be $8.4 \times 10^5$ (R = H) and $1.8 \times 10^7$ $M^{-1}$ $s^{-1}$ (R = Me) [38b]. The differences between the two methods have been attributed to temperature and solvent effects.

## 7. Reactions of photogenerated radicals

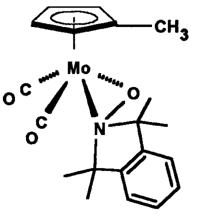
The solution photochemistry of **2** and **3** with visible light, and the thermal chemistry of **1** are dominated by M–M homolysis to yield 17-electron radicals. The reactions of these radicals have been the focus of a substantial literature. As such we shall examine only the major features of this chemistry.

### *7.1. Radical recombination and cross-coupling reactions*

Homolysis of M–M and M–M′ bonds is known to result in formation of metal based radicals. By photolyzing mixtures of homobimetallic compounds it is possible to prepare a range of cross-coupling heterobimetallic derivatives [39]. Early attempts to establish the mechanism of the formation of the triply bonded compounds, $M_2(CO)_4(\eta^5\text{-}C_5H_5)_2$, were complicated by the formation of cross-coupling products during photolysis leading to the erroneous conclusion that radicals were involved in the formation of these species [40]. Later studies established that a CO-loss mechanism was actually involved in this reaction [41].

### *7.2. Reactions with halogenated solvents and radical traps*

In 1975, Ginley and Wrighton established that photolysis of **2** or **3** in halogenated solvents resulted in formation of $M(CO)_3(\eta^5\text{-}C_5H_5)Cl$ in high yield [25b]. By analogy with earlier work on the photolysis of $Re_2(CO)_{10}$, these workers concluded that a radical intermediate was likely involved in the halogenation reaction [42]. The kinetics of the photochemical reaction of **3** with halocarbons was examined and found to be consistent with a radical intermediate [43]. Recent work has established that $M(CO)_3(\eta^5\text{-}C_5H_5)$ ($M = Mo$ or W) radicals react with organic and inorganic halides and pseudohalides by an atom-transfer mechanism rather than electron transfer followed by halogen transfer [44]. The dependence of rate of halogen abstraction on the nature of the halogen ($RI > RBr > RCl$) and the nature of the organic group (benzyl > allyl > 3° > 2° > 1° > $CH_3$) supports an atom-transfer mechanism as does the insensitivity of the reaction to the presence of low concentrations of Lewis base, such as $PPh_3$. The Mo radical is slightly less reactive than the W radical despite higher self-exchange rates for $M(CO)_3(\eta^5\text{-}C_5H_5)/M(CO)_3(\eta^5\text{-}C_5H_5)Cl$ couples [45]. The difference between Mo and W was attributed to the relative bond strengths of Mo–X and W–X [46].



**21**

The rates of reaction between $Cr(CO)_3(\eta^5\text{-}C_5H_5)$ and organic halides have been measured and are also consistent with direct halogen atom abstraction as with the radicals of molybdenum and tungsten. It was concluded that electron transfer processes are not a significant factor in the reaction [47].

The nitroxide radical trap 1,1,3,3-tetramethylisoindoline-2-oxyl, TMIO, has been found to react with $Mo(CO)_3(\eta^5\text{-}C_5H_4CH_3)$ radicals at a rate 77 times faster than Cl atom abstraction from $CCl_4$ to give the complex **21** [48]. $Mo(CO)_3(\eta^5\text{-}C_5H_5)$ and $Mo(CO)_2(PPh_3)(\eta^5\text{-}C_5H_5)$ radicals have been trapped with 2,3,5,6-tetramethyl-1-nitrosobenzene [49]. Both TMIO and $CCl_4$ were used to determine values of $K_{eq} = 1.1 \pm 0.1 \times 10^{-17}$ for the dark reaction:

$$Mo_2(CO)_6(\eta^5\text{-}C_5H_4CH_3)_2 \rightleftharpoons 2Mo(CO)_3(\eta^5\text{-}C_5H_4CH_3)$$

### *7.3. Reactions of radicals with Lewis bases*

In 1968, Haines et al. reported the first photochemical reactions of **2** [50]. UV photolysis of **2** with a variety of phosphines and phosphites gave a set of products

$$Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2 \rightarrow 2\ Mo(CO)_3(\eta^5\text{-}C_5H_5) \qquad \text{photolysis}$$

$$Mo(CO)_3(\eta^5\text{-}C_5H_5) + L \rightleftharpoons Mo(CO)_3L(\eta^5\text{-}C_5H_5) \qquad \text{19-electron intermediate}$$

$$Mo(CO)_3L(\eta^5\text{-}C_5H_5) + Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2 \rightarrow [Mo(CO)_3L(\eta^5\text{-}C_5H_5)]^{+1} + [Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2]^{-1}$$

$$[Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2]^{-1} \rightarrow Mo(CO)_3(\eta^5\text{-}C_5H_5) + [Mo(CO)_3(\eta^5\text{-}C_5H_5)]^{-1}$$

Scheme 2.

including $Mo_2(CO)_5L(\eta^5\text{-}C_5H_5)_2$ where $L = PPh_3$, P(cyclohexyl)$_3$ and $P(OPh)_3$, $Mo_2(CO)_4L_2(\eta^5\text{-}C_5H_5)_2$ where $L = PPh_3$, $P(OPh)_3$, and $P(OBu)_3$, and the ionic products, $[Mo(CO)_2L_2(\eta^5\text{-}C_5H_5)][Mo(CO)_3(\eta^5\text{-}C_5H_5)]$ where $L = PPh_3$, $PEt_3$, and $PBu_3$. Reaction with diphos gave the ionic compound $[Mo(CO)_2(\text{diphos})_2(\eta^5\text{-}C_5H_5)][Mo(CO)_3(\eta^5\text{-}C_5H_5)]$. Subsequent work established that alkyl phosphites also lead to the formation of ionic compounds [51]. The monosubstituted compounds were typically isolated in low yield and were reported to be unstable to light.

Considerable effort has gone into developing an understanding of the mechanism of these reactions. Complicating the interpretation of the photochemical data has been the question of the relative importance of radical versus CO-loss pathways, the misassignment of the *gauche* to *anti* transformation in flash photolyses to a CO recapture process, an abundance of minor products, and the solvent dependence of the back reaction from ionic products to starting materials [52]. Although CO loss is observed for both **2** and **3** upon photolysis into the lower energy electronic transitions in matrices, it is likely that this process is unimportant in solution studies. It now seems that photochemical studies using $\lambda_{irr} > 450$ nm are almost exclusively probing the radical pathway.

Tyler and coworkers have extensively examined the photochemistry of **2**, **3**, and the analogous iron compound, $Fe_2(CO)_4(\eta^5\text{-}C_5H_5)_2$, and established the mechanism presented in Scheme 2 to explain the relevant observations [53]. The central feature of this mechanism is the formation of a 19-electron intermediate that serves as a powerful reductant in subsequent steps. Several reviews have examined the literature up to 1991 [2a,54] and new observations, to be examined below, have served to strengthen the case for a mechanism involving 19 (or $18 + \delta$) electron species. An alternate mechanism proposed by us, Scheme 3, involving photochemical heterolysis of $M_2(CO)_5L(\eta^5\text{-}C_5H_5)_2$ species may be relevant in high-energy photolyses where the CO-loss pathway is significant [55]. High-energy photolysis ($\lambda_{irr} = 290$ nm) of $Mo_2(CO)_5(PPh_3)(\eta^5\text{-}C_5H_5)$ in the presence of $PPh_3$ has been shown to form the ionic products $[Mo(CO)_2(PPh_3)_2(\eta^5\text{-}C_5H_5)]^+$ and $[Mo(CO)_3(\eta^5\text{-}C_5H_5)]^-$ although

$$Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2 \rightarrow Mo_2(CO)_5(\eta^5\text{-}C_5H_5)_2 + CO \qquad \text{photolysis}$$

$$Mo_2(CO)_5(\eta^5\text{-}C_5H_5)_2 + L \rightarrow Mo_2(CO)_5L(\eta^5\text{-}C_5H_5)_2$$

$$Mo_2(CO)_5L(\eta^5\text{-}C_5H_5)_2 \rightarrow [Mo(CO)_2L(\eta^5\text{-}C_5H_5)]^{+1} + [Mo(CO)_3(\eta^5\text{-}C_5H_5)]^{-1} \qquad \text{photolysis or thermolysis}$$

$$[Mo(CO)_2L(\eta^5\text{-}C_5H_5)]^{+1} + L \rightarrow [Mo(CO)_2L_2(\eta^5\text{-}C_5H_5)]^{+1}$$

Scheme 3.

it is not known whether this reaction proceeds by homo- or heterolysis of the Mo–Mo bond [56].

A mechanism similar to that in Scheme 2 has been proposed to account for the photochemical reaction of **2** with halide and pseudohalide ions to yield $Mo(CO)_3(\eta^5\text{-}C_5H_5)X$, where X = Cl, Br, and SCN [57].

$$Mo(CO)_3(\eta^5\text{-}C_5H_5) + Cl^- \rightleftharpoons Mo(CO)_3(\eta^5\text{-}C_5H_5)Cl^- \quad (3)$$

In fact, experiments to determine the $\Delta G°$ of Eq. (3) have found that $\Delta G°$ (Cl) $\leq -2.2$ kcal mol$^{-1}$ and $\Delta G°$ (Br) $\leq -2.5$ kcal mol$^{-1}$ and $\Delta G°$ (I) $\leq -3.1$ kcal mol$^{-1}$ indicating that the formation of the 19-electron species is thermodynamically favorable at r.t. The driving force for this process is attributed to M–X bond formation.

An examination of the non-photochemically initiated reaction of $W(CO)_3(\eta^5\text{-}C_5H_5)$ with phosphines developed kinetic evidence for an associative pathway in this process as well, although the data were unable to distinguish between substitution involving a 19-electron intermediate and a 19-electron transition state [58].

Support for the enhanced reducing ability of 19-electron species has come from rate studies of the reduction of the ferrocinium ion by photochemically generated $W(CO)_3(\eta^5\text{-}C_5H_5)$ radicals [59]. In the absence of phosphine this rate is found to be $k = 1.89(4) \times 10^7$ l mol$^{-1}$ s$^{-1}$ while in the presence of $PPh_3$ the rate increases to $k = 3.0 \times 10^9$ l mol$^{-1}$ s$^{-1}$. The increase in rate has been attributed to formation of the more strongly reducing 19-electron species. The 17-electron species $W(CO)_2(PPh_3)(\eta^5\text{-}C_5H_5)$ forms too slowly under the experimental conditions for it to be a viable alternative reducing agent in this reaction although it may be an intermediate in the formation of $W_2(CO)_5(PPh_3)(\eta^5\text{-}C_5H_5)_2$ and $W_2(CO)_4(PPh_3)_2(\eta^5\text{-}C_5H_5)_2$. $W(CO)_2(PPh_3)(\eta^5\text{-}C_5H_5)$ is estimated to be $1.6 \times 10^2$ times more reactive toward ferrocinium than $W(CO)_3(\eta^5\text{-}C_5H_5)$ [59].

Solutions of $Ru_3(CO)_{12}$ and $PMe_2Ph$ are unreactive, but photolysis of these solutions containing **2** resulted in reduction of the ruthenium compound and formation of $Ru_3(CO)_{11}(PMe_2Ph)$ [60].

Chromium radicals, $Cr(CO)_3(\eta^5\text{-}C_5H_5)$, have been found to react with monodentate and bidentate phosphines to give substitution products of the form $Cr(CO)_2(PR_3)(\eta^5\text{-}C_5H_5)$ and ionic products, $[Cr(CO)_2(diphos)(\eta^5\text{-}C_5H_5)][Cr(CO)_3(\eta^5\text{-}C_5H_5)]$ paralleling the chemistry of the molybdenum and tungsten radicals [61].

## 8. Stabilization of 19 $(18 + \delta)$ species

Given that 19-electron $M(CO)_3(\eta^5\text{-}C_5H_5)L$ radicals have favorable kinetics and thermodynamics of formation, the question remains as to how the odd electron is distributed within the molecule. A number of groups have examined the reactions of these radicals with organic ligands and have used EPR measurements to estimate the distribution of unpaired electron density on the metal and organic fragment. A simple MO model of the binding in these systems predicts that spin density

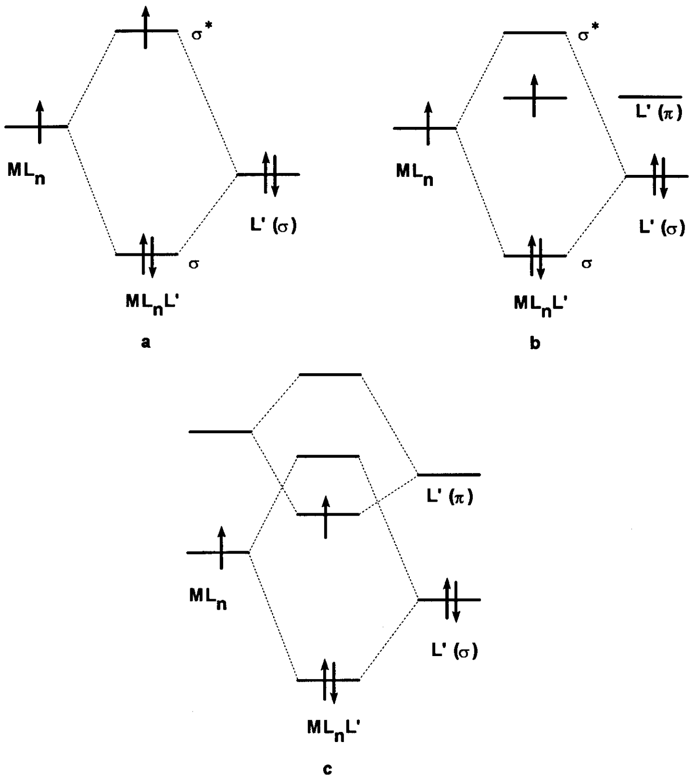


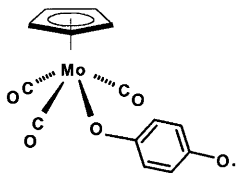
Fig. 3. MO scheme for the interaction of a 17-electron metal fragment with a σ-donor ligand, L′. (a) Ligand has no low-lying vacant orbitals, unpaired electron density is in metal-like orbital. (b) Ligand has low-lying π*-orbital, unpaired electron is predominantly located on the ligand. (c) Ligand and metal have orbitals with the correct symmetry for interaction. The proportion of unpaired electron density on the metal is determined by the relative energies of these orbitals [62].

distribution in these compounds will depend upon the relative energies of the metal orbitals and π* orbitals on the ligand, Fig. 3 [62]. Professor Ted Brown has termed these '$18+\delta$' species in which $\delta$ represents the proportion of electron density residing on the metal while the remaining spin density resides on the ligands. The literature on 19-electron complexes has been reviewed by Tyler and Mao [2b] and Astruc [63].

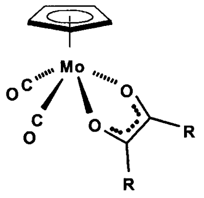
With *p*-benzoquinone and related compounds $Mo(CO)_3(\eta^5\text{-}C_5H_5)$ yields O-bound complexes, **22** [64], while $W(CO)_3(\eta^5\text{-}C_5H_5)$ reacts with *p*-benzoquinone under similar conditions to yield both O- and C-bound species in THF and toluene, respectively [65].

Electron density in the Mo complexes resides predominantly on the ligand, while some spin density is found on the metal in the W complexes. The differences between the Mo and W complexes is consistent with the MO model since the atomic orbitals of W are higher in energy than those of Mo, thus shifting spin density to the metal.

Complexes between Mo radicals and *o*-quinones yield bidentate quinone compexes, **23**, while those of W form an observable monodentate complex as well as a bidentate species. Spin density for the $Mo(CO)_2(\eta^5\text{-}C_5H_5)$(*o*-quinone) species is dominantly on the ligand [66] while more spin density is observed on the metal in both W and $Mo(CO)_2(\eta^5\text{-}C_5H_4CH_3)$(*o*-quinone) complexes [67]. Ligand-based radicals are also found with bidentate O,N radical traps [68].



**22**



**23**

A series of ligands incorporating diphosphine groups have been examined. 2,3-Bis(diphenylphosphino)maleic anhydride forms a monodentate complex with $Mo(CO)_3(\eta^5\text{-}C_5H_4CH_3)$ that thermally loses ligand to reform $Mo_2(CO)_6(\eta^5\text{-}C_5H_4CH_3)_2$. Some bidentate compound is formed as evidenced by the appearance of a weak triplet in the ESR spectrum of the solution. In contrast, the highly sterically encumbered radical, $Mo(CO)_3(\eta^5\text{-}C_5HPh_4)$ forms an isolable bidentate complex with the ligand [69].

Examination of a series of ligands established that ligands with reduction potentials more positive than $-1$ V (vs. SCE) formed long-lived $18+\delta$ complexes, while those with potentials more negative than $-1$ V formed reactive $18+\delta$ complexes. These results parallel the predictions of the simple MO diagram presented above which suggest that the relative energies of metal orbitals and ligand $\pi^*$ orbitals determines the distribution of spin density within the molecule [62].

## 9. The role of CO loss intermediates

Although it may appear from the preceding discussion that the photochemistry of **2** and **3** is dominated by the reactions of the radicals, the CO-loss pathway also plays an important role in the chemistry of these compounds. Early studies of the formation of the triply bonded compounds $M_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ postulated a mechanism involving dimerization of $M(CO)_2(\eta^5\text{-}C_5H_5)$ species formed by CO loss from $M(CO)_3(\eta^5\text{-}C_5H_5)$ radicals. Studies on the reaction of CO with $M_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ ruled out such a pathway on the basis of microscopic irreversibility, and the recent time-resolved IR studies have clearly established that the CO-loss species, $M_2(CO)_5(\eta^5\text{-}C_5H_5)_2$, is the true intermediate for formation of the triply bonded compounds [36,37,41].

Whether $Mo_2(CO)_5(\eta^5\text{-}C_5H_5)_2$ is the intermediate in the observed formation of $Mo_2(CO)_5L(\eta^5\text{-}C_5H_5)_2$ as a minor product in the photolyses of **2** with various phosphine and phosphite ligands is not clear since this compound could also arise from radical pathways. The observation that $M_2(CO)_5(\eta^5\text{-}C_5H_5)_2$ is long lived in solution at 200 K suggests that low temperature photolysis might be used to build synthetically significant concentrations of $M_2(CO)_5(\eta^5\text{-}C_5H_5)_2$ that might then be reacted with ligand after a dark period to permit the concurrently formed radicals to recombine.

The situation is much clearer with the ring coupled compounds. For these compounds there is no evidence of radical formation and the observed photochemistry appears to be entirely accounted for by CO-loss processes.

Photolysis of **8** and **9** with either $PPh_3$ or $PMe_3$ yields both mono, **24**, and disubstituted, **25**, derivatives. Unlike their non-ring coupled analogs, these compounds are stable, even in air, for extended periods and show no evidence of decomposition with light [55].

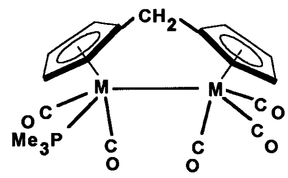
Photolysis of **14** with phosphines or phosphites does not result in product formation. Phosphine and phosphite derivatives of **14** may be prepared indirectly by initial synthesis of $[Mo(CO)_2LX]_2(\eta^5,\eta^5\text{-}C_5H_4\text{–}C_5H_4)$, where $L = PPh_3$, $PCy_3$, $PMe_3$ and $X = H$, Cl, Br, or I, followed by either abstraction of H using the trityl radical or reduction of the halides using sodium dispersion [70]. $Mo_2(CO)_4(PMe_3)_2(\eta^5,\eta^5\text{-}C_5H_4\text{–}C_5H_4)$ has also been prepared by photoloysis of $[Mo(CO)_2(PMe_3)H]_2(\eta^5,\eta^5\text{-}C_5H_4\text{–}C_5H_4)$ [71]. The molecular structure of $Mo_2(CO)_4(PMe_3)_2(\eta^5,\eta^5\text{-}C_5H_4\text{–}C_5H_4)$ has been reported and it has been found that the molecule twists significantly from fulvalene planarity [72].

The Mo–Mo bond lengths of $Mo_2(CO)_4(PMe_3)_2(\eta^5,\eta^5\text{-}C_5H_4\text{–}CH_2\text{–}C_5H_4)$ (Mo–Mo = 3.1341 Å) and $Mo_2(CO)_4(PMe_3)_2(\eta^5,\eta^5\text{-}C_5H_4\text{–}C_5H_4)$ (Mo–Mo = 3.220 Å) are both *shorter* than those of the unsubstituted compounds. In the absence of good theoretical models for these compounds, we speculate that $PMe_3$, being a poorer $\pi$-acid, allows greater electron density in those orbitals that form the Mo–Mo bond.

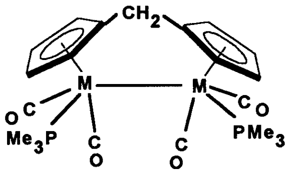
Exposure of $Mo_2(CO)_4(PPh_3)_2(\eta^5,\eta^5\text{-}C_5H_4\text{–}C_5H_4)$ to light in the presence of organohalides results in the formation of $[Mo(CO)_2(PPh_3)X]_2(\eta^5,\eta^5\text{-}C_5H_4\text{–}C_5H_4)$ by what is believed to be photochemical bond homolysis. Recombination of the radicals may be hindered by the steric demands of the $PPh_3$ that would favor rotation about the C–C bond of the fulvalene to give the diradical, $[Mo(CO)_2(PPh_3)]_2(\eta^5,\eta^5\text{-}C_5H_4\text{–}C_5H_4)$, in its *anti* conformation [70b].

Photolysis of **8** or **9** with alkynes gives the expected tetrahedrane compounds, $M_2(CO)_4(\text{alkyne})(\eta^5,\eta^5\text{-}C_5H_4\text{–}CH_2\text{–}C_5H_4)$ (**26**), where alkyne = $C_2H_2$, $PhC_2H$, $C_2Ph_2$. Since there is no evidence for formation of a triply bonded intermediate analogous to $M_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ with this class of compounds the mechanism for acetylene addition may proceed through an $\eta^2$-alkyne complex followed by rearrangement [73].

Photochemical reaction of **14** with alkynes gives the expected tetrahedrane derivatives, $Mo_2(CO)_4(\text{alkyne})(\eta^5,\eta^5\text{-}C_5H_4\text{–}C_5H_4)$, as well as an unusual doubly substituted product, $Mo_2(CO)_3(\text{alkyne})_2(\eta^5,\eta^5\text{-}C_5H_4\text{–}C_5H_4)$ (**27**), containing both a $\mu$-alkyne and an $\eta^2$-alkyne [74]. A similar reaction with **15** gave no simple tetrahedrane compound, but did give an $\eta^2$-alkyne compound $W_2(CO)_5(\eta^2\text{-alkyne})(\eta^5,\eta^5\text{-}C_5H_4\text{–}C_5H_4)$ (**28**), and a doubly substituted compound similar to that formed by **14** [75].



**24**



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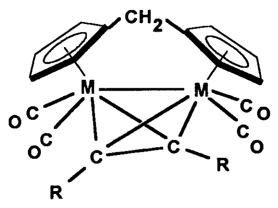
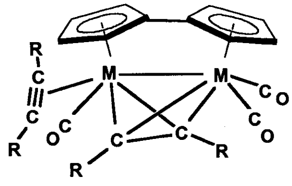
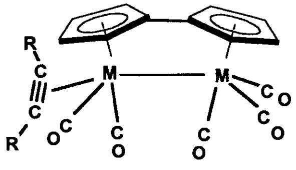


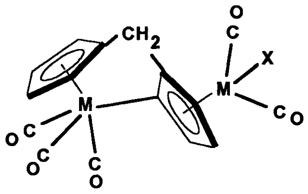
**26**



**27**

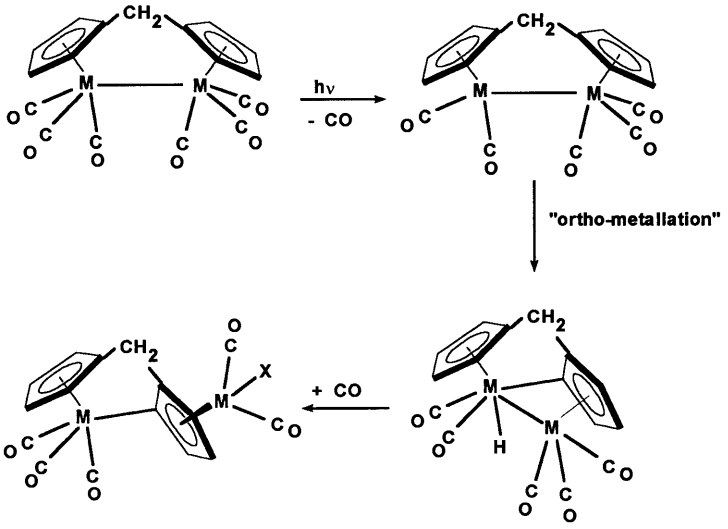


**28**



**29, X = H; 30, X = Cl**

In the absence of Lewis bases, photolysis of **8** and **9** results in the formation of 'twist' compounds, **29**, X = H, in which a C–H from one cyclopentadienyl ring has oxidatively added to the adjacent metal atom, followed by reductive elimination of M–H and recapture of CO Scheme 4. Reaction of the metal hydrides with $CH_2Cl_2$ results in halide for hydride exchange and the isolable chloride derivatives, **30**, X = Cl. Compound **30** forms directly when the photolysis is carried out in $CCl_4$. There is no evidence for formation of $[M(CO)_3Cl]_2(\eta^5,\eta^5\text{-}C_5H_4\text{–}CH_2\text{–}C_5H_4)$ in this photolysis ruling out a significant radical pathway in these ring coupled compounds. The reaction is analogous to the well-known orthometallation reaction [76]. We have reported the formation of similar 'twist' compounds for $Ru_2(CO)_4(\eta^5,\eta^5\text{-}C_5H_4\text{–}CH_2\text{–}C_5H_5)$ [77]. An analogous reaction has been reported for $M_2(CO)_4(DPPM)(\eta^5\text{-}C_5H_5)_2$, where M = Mo and W [78].



Scheme 4.

## 10. Conclusions

Compounds **2** and **3** have two distinct photochemical pathways, M–M bond homolysis and CO-loss that are strongly wavelength sensitive. Although extensive studies of the bond homolysis pathway and the fate of the radicals has been carried out, far less is known about the chemistry of the CO-loss pathway and this appears to be a potentially fruitful area for exploration. Ring coupling appears to suppress either thermal or photochemical M–M bond homolysis, thus these compounds are excellent platforms for examining the CO pathway free of interference. In particular, the ring-coupled chromium derivatives present interesting targets for examining whether there is a CO-loss pathway for these compounds and further investigation of the effect of ring-coupling on the stability of the Cr–Cr bond.

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