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Photochemistry and reaction intermediates of the bimetallic Group VIII cyclopentadienyl metal carbonyl compounds, (η^5-C_5H_5)$_2$$M_2(CO)_4$ and their derivatives

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Contents

Abstract

The bonding, structures and photochemistry of the Group VIII metal cyclopentadienyl carbonyl derivatives of the form, (η^5-C_5H_5)$_2$$M_2(CO)_4$, where M = Fe, Ru and Os, are reviewed. The primary emphasis of the review is to bring together the somewhat complex literature in this field, to critically examine the evidence and interpretations and to

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identify areas for future research opportunities.

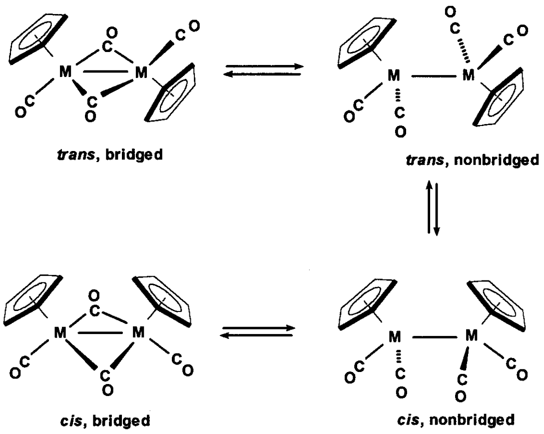
Keywords: Photochemistry; Reaction intermediates; Group VIII; Cyclopentadienyl metal carbonyl compounds

1. Introduction

The family of compounds, $(\eta^5\text{-}C_5H_5)_2M_2(CO)_4$, where M = Fe (**I**), Ru (**II**) and Os (**III**), are among the oldest and are perhaps the second most studied class of organometallic derivatives after the progenitor of all organometallic compounds, ferrocene. **I** was first reported by Piper and Wilkinson in 1956 [1], while its ruthenium [2] and osmium [3] analogues were first described by Fischer and co-workers in 1962. Although excellent modern syntheses are available for **II** [4], the chemistry of **III** is still largely undeveloped because of the cost and the relatively low yields of the several steps of the syntheses [5]. In fact, there appear to be no papers on **III** published in the 1990s. The large synthetic photochemistry of the iron and ruthenium compounds stimulated efforts at understanding the mechanistic details and intermediates involved in these reactions. Over the intervening years techniques of increasing sophistication have been brought to bear on these questions. The photochemistry of **I** has become a reference reaction for new methods and as such its photochemistry is understood at an unusually detailed level. In this issue examining *Organometallic Chemistry at the Millennium* it is particularly appropriate to review critically review literature on these compounds and their derivatives in the hope of bringing together what is known and with an eye toward stimulating future research to fill in the remaining gaps in our knowledge.

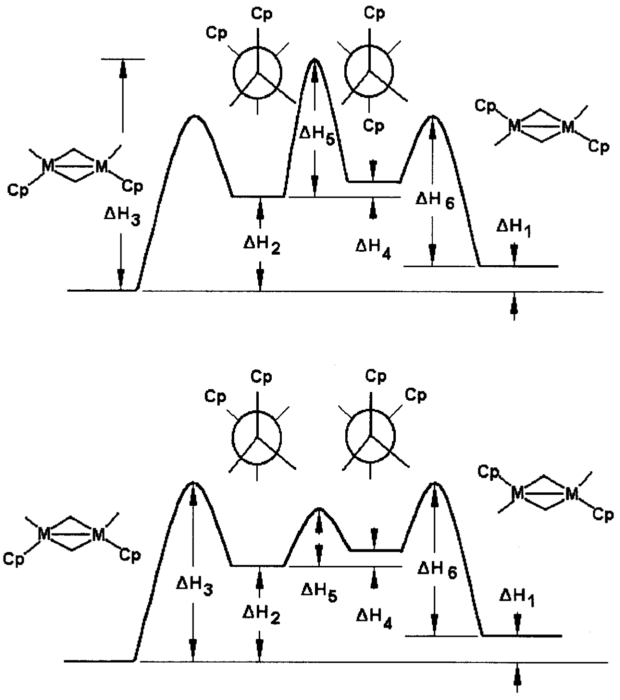
2. Structure and bonding

I and **II** exist in solution as a set of species illustrated in Scheme 1. Isomers having all-terminal carbonyl groups are in equilibrium with those having bridging carbonyl groups. In general, **I** predominantly ($>99\%$) exists in solution in its bridging conformations, **II** is found to be in equilibrium with its all-terminal and bridging forms and **III** is only found in its all-terminal conformation [6]. A number of studies employing IR [7], Raman [8], UV–vis [9] and NMR [10] spectroscopic techniques have established that the equilibria for **I** and **II** depend upon temperature, solvent polarity and pressure. For **I** and **II**, low temperatures favor the bridged conformers [4e,5b] and polar solvents favor *cis* conformers. The NMR studies of the equilibrium processes for **I** are particularly elegant and permitted a detailed analysis of the energies of the reaction coordinate shown in Scheme 2. A similar study employing both ^{1}H- and ^{13}C-NMR clarified further details of these processes and provided energies for the reaction coordinate diagram of **II** [11]. Energy of activation data are presented in Table 1.



Scheme 1. *Cis*/*trans* equilibrium for **I** and **II**.

Introduction of alkyl substituents onto the cyclopentadienyl rings for both iron and ruthenium derivatives increases the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the bridge to terminal carbonyl exchange as a consequence of increased electron donation into the μ-CO



Scheme 2. Potential energy vs. reaction coordinate for structural interconversions in **I** (top) and **II** (bottom) [11a].

Table 1
Enthalpy of activation (kcal mol^{-1}) for structural interconversions of **I** and **II** [11a]

Compound	ΔH_1	ΔH_2	ΔH_3	ΔH_4	ΔH_5	ΔH_6
I	1.3	4.9	11.1	<0.2	6.2	6.5
II	~1	2.6	8.1	<0.2	<5	7.6

backbonding orbitals [11a]. One or two substituents do not appear to have a significant impact on the *cis*/*trans* ratio [7g,12] however $(\eta^5\text{-}1,3\text{-}t\text{-}Bu_2C_5H_3)_2Fe_2(CO)_4$ is reported to favor the *cis* form in solution [13]. Tetra- and penta-substituted rings generally favor *trans* bridged forms [14]. For example, $[\eta^5\text{-}C_5(CH_3)_5)]_2M_2(CO)_4$, where M = Fe(IV) or Ru(V) and $[\eta^5\text{-}C_5(CH_3)_4(C_2H_5)]_2Ru_2(CO)_4$ prefer the *trans* bridged conformations [15]. An analysis of *cis*/*trans* ratios of a series of iron compounds with pairings of C_5H_5, $C_5(CH_3)_4H$ and $C_5(CH_3)_5$, rings established that the critical steric factor in these compounds appears to be the number of methyl groups that interact over the metal–metal bond (the position of closest inter-ring contact) in the *cis* configuration.

The molecular structures of both the *cis* [16] and *trans* [17] bridged forms of I and the *trans* bridged form of **II** [18] have been reported. The molecular structure of a sterically encumbered, 1-methyl, 3-phenyl, derivative of **II** is presented in Fig. 1 [19]. Coupling of the cyclopentadienyl rings by a variety of bridging groups has been reported and this coupling constrains the molecules to a *cis* geometry [21,22].

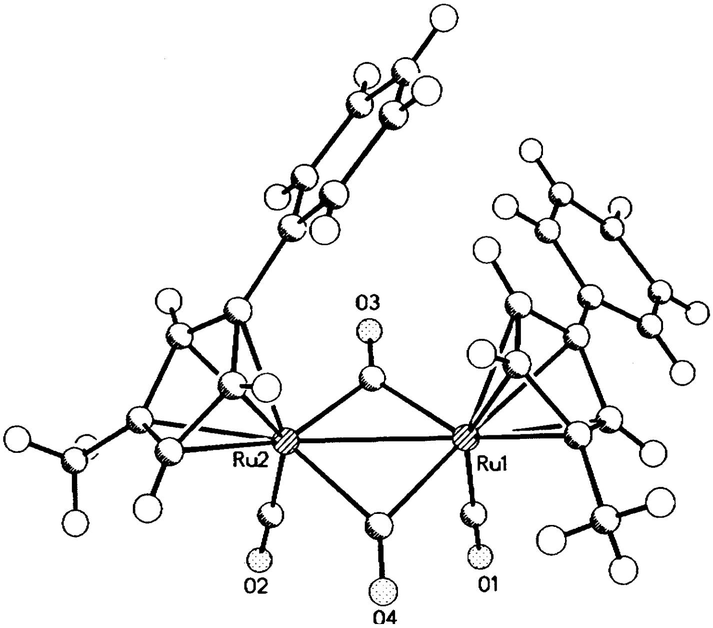


Fig. 1. Molecular structure of $[1,3\text{-}\eta^5\text{-}C_5H_3(CH_3)(C_6H_5)]_2Ru_2(CO)_2(\mu\text{-}CO)_2$.

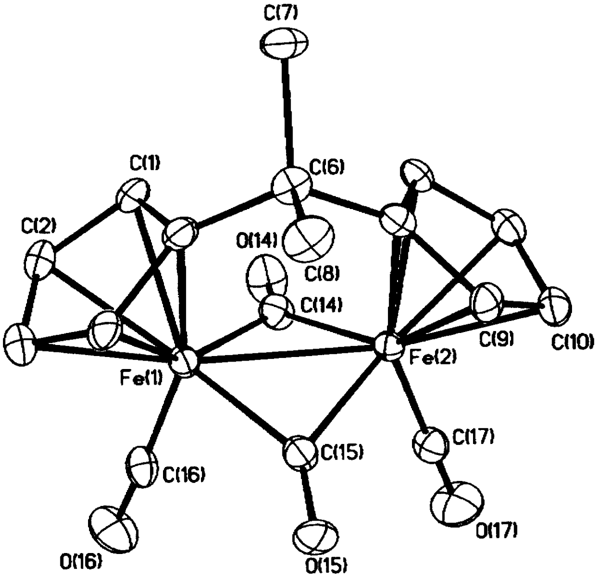


Fig. 2. Molecular structure of [η^5-η^5-C_5H_4-$C(CH_3)_2$-C_5H_4]$Fe_2(CO)_2(\mu\text{-}CO)_2$.

The molecular structures of $Fe_2(CO)_4[\eta^5,\eta^5\text{-}C_5H_4C(CH_3)_2C_5H_4]$ [22] and the 2,3-isomer of $Ru_2(CO)_4[\eta^5,\eta^5\text{-}(CH_3O_2C)C_5H_3C_5H_3(CO_2CH_3)]$ [23] are presented in Figs. 2 and 3. The Fe–Fe and Ru–Ru bond lengths of a series of representative compounds are presented in Table 2. Coupling the cyclopentadienyl rings by one or two carbons has the effect of slightly reducing the M–M bond length, whereas direct coupling of the cyclopentadienyl rings to give fulvalene derivatives results in elongation of the M–M bond lengths [21c,23].

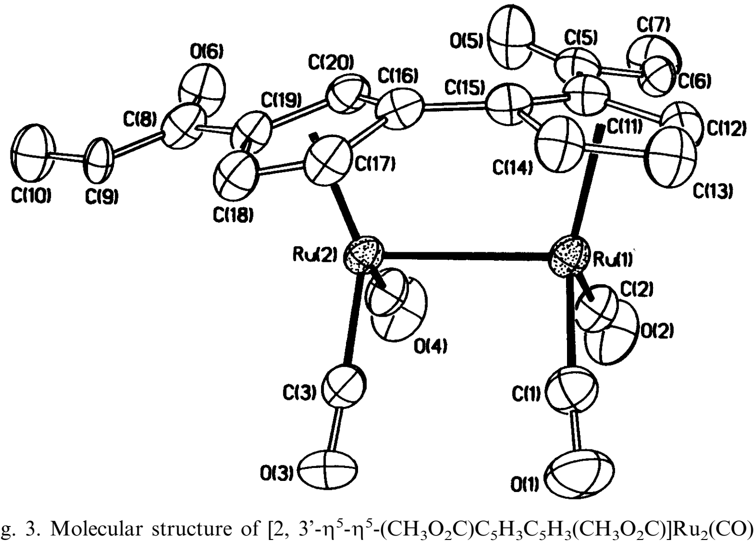


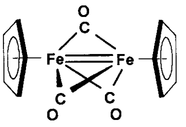
Fig. 3. Molecular structure of [2, 3'-η^5-η^5-$(CH_3O_2C)C_5H_3C_5H_3(CH_3O_2C)$]$Ru_2(CO)_4$.

Table 2
Representative Fe–Fe and Ru–Ru bond lengths (Å)[a]

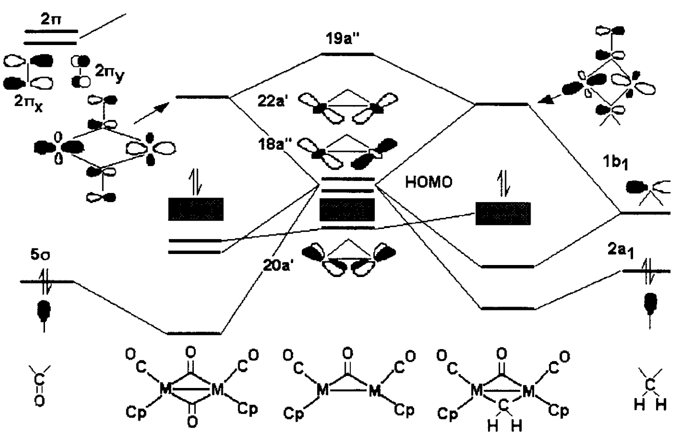
Compound	M–M bond length	Ref.
trans-$Cp_2Fe_2(CO)_2(\mu\text{-}CO)_2$ (**I**)	2.534(2)	[17]
cis-$Cp_2Fe_2(CO)_2(\mu\text{-}CO)_2$ (**I**)	2.531(2)	[16a]
cis-$(Cp\text{-}SiMe_2\text{-}Cp)Fe_2(CO)_2(\mu\text{-}CO)_2$ (**XIII**)	2.512(3)	[20d]
cis-$(Cp\text{-}CH(NMe_2)CH(NMe_2)\text{-}Cp)Fe_2(CO)_2(\mu\text{-}CO)_2$	2.510(1)	[20e]
cis-$(Cp\text{-}Ge_2Me_2\text{-}Cp)Fe_2(CO)_2(\mu\text{-}CO)_2$	2.544(3)	[20b]
cis-$(Cp\text{-}Si_2Me_4\text{-}Cp)Fe_2\ (CO)_2(\mu\text{-}CO)_2$	2.526(2)	[20c]
$Cp_2^*Fe_2(\mu\text{-}CO)_3$ (**VII**)	2.265(1)	[47]
trans-$Cp_2Ru_2(CO)_2(\mu\text{-}CO)_2$ (**II**)	2.7377(5)	[18]
trans-$(C_5Me_4Et)_2Ru_2(CO)_2(\mu\text{-}CO)_2$	2.7584(5)	[15c]
cis-$(Cp\text{-}SiMe_2\text{-}Cp)Ru_2(CO)_2(\mu\text{-}CO)_2$ (**XVI**)	2.704	[21a]
cis-$(Cp\text{-}CH_2\text{-}Cp)Ru_2(CO)_2(\mu\text{-}CO)_2$ (**XII**)	2.766(1)	[21b]
cis-$(Cp\text{-}Cp)Ru_2(CO)_2(\mu\text{-}CO)_2$ (**XVII**)	2.821(1)	[21d]
trans-$Cp_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe_2)$	2.712(1)	[92c]
$Cp_2Ru_2(\mu\text{-}CO)(\mu\text{-}\eta^{2:2}\text{-}Ph_2C_2)$ (**XXII**)	2.505(1)	[89]

[a] $Cp = C_5H_5$, $Cp^* = C_5Me_5$.

The use of Raman spectra on metal–metal bonded compounds is complicated by photochemical side reactions. Onaka and Shriver employed a 514.5 nm excitation to study the Raman spectra of **II** and observed a band at 217 cm^{-1} in the solid state and bands at 221 and 180 cm^{-1} in solution. These bands were assigned to the bridged and nonbridged forms of **II**, respectively. No bands attributable to the Fe–Fe bond stretch were observed in an examination of **I** by these workers although a later study by San Fillippo and Sniadoch did observe a band at 226 cm^{-1} that they attributed to an Fe–Fe stretching mode. In the last few years significant improvements in the available excitation wavelengths and increases in sensitivity of instrumentation have allowed a set of studies on **I** and **IV**. Vitale et al. [24] have examined **I** and **IV** in cyclohexane solution, while Fickert et al. [25] have examined **I** in the solid state and in a krypton matrix at 20 K. A third study by Diana et al. [26] focused primarily on Raman and IR spectral analysis of the vibrational modes of the cyclopentadienyl ligands of **I** in its crystalline form. Vitale, Fickert and their co-workers have obtained roughly equivalent results with ν(Fe–Fe) at 225 and 140 cm^{-1} for **I** and **IV**, respectively. The significant shift to lower frequency for **IV** is attributed to coupling between the iron atoms and the heavy pentamethylcyclopentadienyl ligands. Resonance Raman spectra recorded at 514.5 nm results in considerable formation of the relatively long-lived, CO-loss species, $(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-}CO)_3$ (**VI**) and $[\eta^5\text{-}C_5(CH_3)_5]_2Fe_2(\mu\text{-}CO)_3$ (**VII**). Symmetric



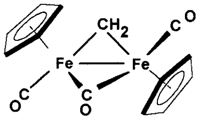
VI



Scheme 3. Molecular orbital diagrams of *cis*-(η^5-C_5H_5)$_2$$Fe_2(CO)_4$ and *cis*-(η^5-C_5H_5)$_2$$Fe_2$(CO)3(μ-$CH_2$) [30].

(A_1') and asymmetric (E′) bands were found at 1877 and 1823 cm^{-1} for **VI** and at 1841 and 1790 cm^{-1} for **VII**. The Fe_2(μ-CO)$_3$ core of the molecules are expected to have two totally symmetric (A_1') modes under D_{3h} symmetry corresponding to an Fe–Fe stretch and an Fe–C breathing mode. Bands at 514 and 214 cm^{-1} and 528 and 142 cm^{-1} have been assigned to these A_1' modes for **VI** and **VII**, respectively.

The nature of the bonding in the bridged forms of **I** and **II** have received considerable attention because of the differences between simple bonding diagrams based on 18 electron rules and less intuitive models that arise from experiment and higher order bonding models. The bridging forms of both **I** and **II** are diamagnetic, thus there is a tendency to illustrate these molecules with a M–M bond [27]. A variety of computational models including extended Hückel [28], ab initio Hartree–Fock [29], Fenske–Hall [30] and density functional theory [31] all agree with experimental data provided by low temperature electron density studies that there is essentially no direct Fe–Fe bonding in **I**. All models suggest the HOMO is delocalized about the Fe_2(μ-CO)$_2$ core of the molecule and, with the exception of the ab initio calculations, suggest a LUMO that is primarily Fe–Fe σ*. The Fenske–Hall molecular orbital diagrams for *cis*, bridged **I** and *cis*-[(η^5-C_5H_5)Fe(CO)]$_2$-(μ-CO)(μ-CH_2) (**VIII**), reported by Bursten and Cayton [30] are reproduced in Scheme 3 and the HOMO orbital diagrams for *trans*, bridged **I** as determined by DFT [31] using a Spartan Pro computational package are presented in Fig. 4. It should be noted that the LUMO and LUMO + 1 arising from DFT calculations



VIII

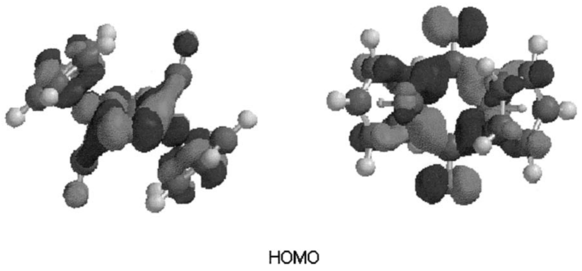
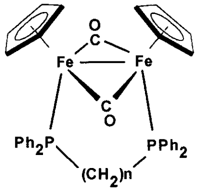


Fig. 4. HOMO orbital diagram for **I**.

also reveal an antibonding component between the iron atoms and the terminal carbonyl groups as would be expected from photochemical results (vide infra). Percentages of iron and CO character in the highest occupied and lowest unoccupied orbitals of **I** as determined by Bursten are presented in Table 3.

Bursten notes that the photoelectron spectra of **I** as reported by Granozzi [28b] support the Fenske–Hall orbital model and that the sharpness of the lowest ionization band is consistent with an essentially nonbonding HOMO. The second lowest broad envelope of bands in the photoelectron spectrum was assigned to MOs with large Fe 3d character.

Further support for the delocalized bonding picture of these compounds comes from the molecular structures of the electronically similar $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)]_2[\mu\text{-}Ph_2P(CH_2)_nPPh_2]$, where $n = 1$ (**IX**), 2 (**X**) [32]. Comparison of the Fe–Fe distance



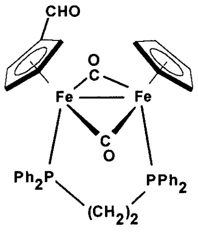
IX: n = 1

X: n = 2

Table 3
Percent characters of the highest occupied and lowest unoccupied orbitals of **I** [30]

Orbital	Type of M–M interaction	%Fe	%CO
$3b_u$ (LUMO)	σ^*	79	11
$2a_g$ (HOMO)	π^*	89	8
$1a_g$	σ/δ	96	0
$2b_g$	π^*	54	36
$1a_u$	δ^*	81	15
$1b_g$	δ	79	17
$2b_u$	π	76	22
$1b_u$	σ^*/δ^*	65	27

of the neutral compound with that of its cation indicate almost no change (less than 0.01 Å) upon oxidation consistent with a delocalized HOMO, but inconsistent with an Fe–Fe σ bond as a HOMO. It is unfortunate that the actual molecular structures upon which these conclusions are based do not seem to have appeared in the literature [33]. The molecular structure of **X** has been reported and the Fe–Fe bond length was found to be 2.516(1) Å while its aldehyde derivative, **XI**, was found to have an Fe–Fe bond length of 2.527(1) Å [34]. The structure of **IX** was also determined by us and is presented in Fig. 5 although an exceptionally large unit cell, almost certainly the same problem encountered by the earlier workers, prevented a full refinement of the data [34b]. Comparing compounds **X** and **XI** we note that introduction of an electron withdrawing aldehyde group onto one of the cyclopentadienyl rings has the effect of increasing the Fe–Fe bond length by 0.011 Å approximately the same change as reported for oxidation.



XI

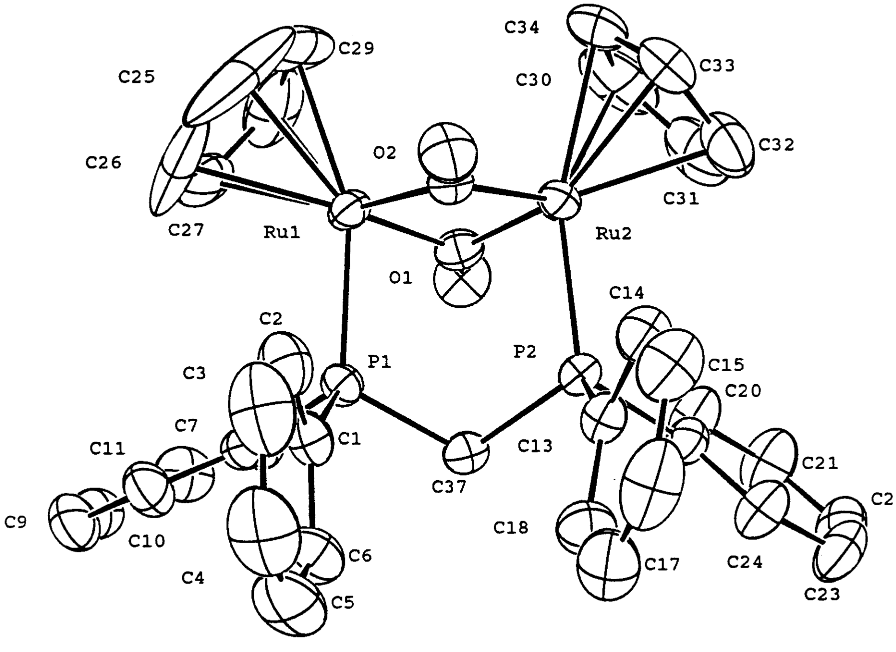


Fig. 5. Molecular structure of $(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-}CO)_2[\mu\text{-}(Ph_2P)_2CH_2]$.

Table 4
Electronic spectral bands of **I**, **II** with spectral assignments

Compound	UV–vis nm (*ε*)	INDO/CI assignment (37) bridged conformers	Other assignments
I	514 (710)	HOMO → LUMO σCO_b-M → σ_d^*	$d_{nb} \rightarrow \sigma^*$ (35)
	410 (1870)	HOMO-1 → LUMO $\sigma_d \rightarrow \sigma_d^*$	$d_{nb} \rightarrow \sigma^*$ (35)
	346 (9190)	HOMO → LUMO+2 $\sigma_b \rightarrow \pi Cp^*$	$\sigma_b \rightarrow \sigma^*$ (35) $\pi \rightarrow \pi^*$ (36)
II	435 (1280)	HOMO → LUMO σCO_b-M → σ_d^*	$\pi_d \rightarrow \sigma^*$ (35)
	330 (13 900)	HOMO → LUMO+2 σCO_b-M → πCp^*	$\sigma_b \rightarrow \sigma^*$ non-bridged (35)
	265 (10 950)	HOMO-1 → LUMO+2 $\delta_d \rightarrow \pi Cp^*$	$\sigma_b \rightarrow \sigma^*$ bridged (35)

These bonding arguments are relevant to the assignment of spectral features in the electronic spectra of **I** and **II**. Electronic spectral bands of **I** and **II** are presented in Table 4. Wrighton and co-workers [35] have noted that the electronic spectrum of **1** is relatively insensitive to solvent and temperature due to its being $>99\%$ bridged in solution. The strong band at 346 nm (benzene) was assigned to a $\sigma_b \rightarrow \sigma^*$ transition. Caspar and Meyer [36] have suggested that in the light of theoretical models this might be better designated as $\pi \rightarrow \pi^*$, but Bursten [30] notes that the calculated energetic separation between the Fe–Fe σ and σ* levels is close to the observed energy of the 346 nm transition. Weak bands observed at 410 and 514 nm may then arise from π(HOMO) → σ* (LUMO) or $d_{nb} \rightarrow \sigma^*$ transitions. INDO/CI calculations have been carried out on both **I** and **II** and these results were used to assign electronic spectra as presented in Table 3 [37].

The electronic spectra of **II** have been found to be sensitive to both temperature and solvent consistent with the equilibrium between bridged and all-terminal forms. The observed transition at 330 nm is attributed to the $\sigma_b \rightarrow \sigma^*$ of the all-terminal form while that at 265 nm is assigned to the $\sigma_b \rightarrow \sigma^*$ of the bridged form [9,35]. No electron density or photoelectron spectroscopic studies been reported on **II**. Density functional calculations for *trans*, bridged **II** using Spartan, while certainly approximate, yield HOMO and LUMO orbitals that are identical to those found for *trans*, bridged **I** [31].

3. Photochemical studies

3.1. Photochemistry of (η^5-C_5H_5)$_2$$Fe_2(CO)_4$ and its derivatives

The earliest application of photochemistry to reactions of **I** appears to be the use of UV irradiation by Cullen and Hayter in 1964 to prepare (η^5-

$C_5H_5)Fe(CO)_2As(CF_3)_2$ and $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2[\mu\text{-}As(CF_3)_2]_2$ [38]. The following year, King and Bisnette used a similar strategy in the reaction of **I** and $S_2(CH_3)_2$ to prepare $(\eta^5\text{-}C_5H_5)Fe(CO)_2SCH_3$, a compound that had defied preparation by thermal methods [39]. Shortly thereafter photochemical methods were employed to prepare thermally unstable phosphine derivatives [40]. In 1975, Giannotti and Merle found that visible light photolysis of solutions of **I** in CCl_4, $CHCl_3$, or $CHBr_3$ resulted in formation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ or $(\eta^5\text{-}C_5H_5)Fe(CO)_2Br$ [41]. Although photochemical metal–metal homolysis reactions were well established [42], the observation by the French workers marked the first example of homolysis for a molecule existing predominantly in a bridged carbonyl form and prompted Wrighton and his co-workers [35] to initiate what was to be the beginning of a 20 year odyssey to establish the mechanisms and intermediates involved in these reactions.

A series of complimentary studies by Wrighton [35], Gray [43] and their co-workers employed classical photochemical methods and quantum yield measurements to examine the photolysis of **I** and **II** at various irradiation wavelengths in the presence of halocarbons, phosphines and CO. These studies provided strong evidence for a radical reaction pathway in the formation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ and also non-radical pathways for phosphine and phosphite substitution. A yellow species believed to be $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\mu\text{-}CO)Fe(CO)L(\eta^5\text{-}C_5H_5)$ was observed to form upon irradiation ($\lambda_{irr} > 500$ nm) of cyclohexane solutions at -78°C. Upon warm-up to room temperature (r.t.) these yellow compounds decomposed to the mono-substituted derivatives, $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)(\mu\text{-}CO)_2L$ [43].

Caspar and Meyer [36] employed flash photolysis with UV–vis detection to examine the photolysis of **I** and found evidence for two intermediates. A short lived intermediate, assumed to be the $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ radical, decayed back to **I** by second order kinetics while a long lived (s) intermediate returned to **I** by first order kinetics. The long lived intermediate was found to have an electronic absorption at 510 nm. The rate of decay of the long lived intermediate was sensitive to the monitoring light intensity. They postulated that this second intermediate was the CO-loss product, $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3$ (**VI**). A third, very long lived (min) intermediate was observed in later studies and will be discussed below.

Almost simultaneously, Rest [44], Wrighton [45] and their co-workers examined the photolysis of **I** in low-temperature CH_4 [44], polyvinyl chloride [44] and hydrocarbon [45] matrices and observed the formation of a new species accompanied by the characteristic band of free CO. The new species had a single band in the bridging carbonyl region at 1812 cm^{-1} and an electronic absorption at 510 nm. These features established the species as being identical to the long lived intermediate observed by Caspar and Meyer [36] and also permitted its assignment as **VI**. One interesting feature noted by both groups was that only the *trans*, bridged isomer of **I** appeared to undergo photochemical CO-loss. Rest et al. [46] later found that *trans*, bridged **I** underwent bridge opening to the all-terminal form upon long wavelength ($\lambda_{irr} > 475$ nm) irradiation. IR bands for the all-terminal form had been reported from solutions studies [7e]. Wrighton [35] has suggested that the differences in the abilities of the *cis* and *trans* isomers to form **VI** are not electronic, but arise from differences in the degree of structural rearrangement to achieve the linear, bridged species **VI**. Upon CO-loss, the *trans* isomer can rearrange with a simple twisting motion, whereas the *cis* isomer must move the bulky cyclopentadienyl rings across a considerable angular change to arrive at a linear form.

Subsequent solution studies by Wrighton et al. [47] found that **VII** could actually be isolated by photolysis of alkane solutions ($\lambda_{irr} = 355$ nm) while vigorously purging the solution with argon. A molecular structure of this compound confirmed the proposed geometry with a C_{3v} core of three bridging carbonyl groups and an Fe–Fe distance of 2.265(1) Å. The puzzling absence of an NMR spectrum was resolved by Bursten who suggested that the molecule was paramagentic (which was later confirmed by experiment) and developed a molecular orbital description revealing a half-filled, doubly degenerate HOMO. The triplet nature of the $(\eta^5\text{-}C_5R_5)_2Fe_2(\mu\text{-}CO)_3$ intermediates has implications to both their rate of formation and reactions with ligands as a spin state change must occur in these processes (vide infra).

The development of time-resolved IR techniques by Poliakoff, Turner and co-workers [48] introduced a powerful new tool to the study of photochemical mechanisms and intermediates. In fact, the refinement of understanding of the photochemistry of **I** since 1984 parallels the evolution of the temporal and spectral resolution of time-resolved IR methods.

Time-resolved IR methods are particularly important in the study of radical intermediates since the mononuclear radicals typically do not have electronic absorption bands in the visible region and cage effects in low temperature matrices results in their rapid recombination. By monitoring the IR spectra of a sample on the microsecond time scale Turner, Poliakoff and co-workers were able to observe directly the formation and decay of **VI** and the $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ radical and confirm both the identities of species and rates reported earlier by Caspar and Meyer [36,49]. One consequence of these studies has been the ability to examine the rates of reaction of **VI** and the $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ radical with a variety of ligands.

Reactions of **VI** with CH_3CN, PBu_3 and PPh_3 were found to be first order in the bimetallic species. The enthalpies of activation for all three ligands are similar suggesting a similar mechanism. The values of the entropy of activation are consistent with those expected of an associative reaction. The entropy of activation for PPh_3 is somewhat larger than for the other two ligands suggesting that steric factors may play a role in the reaction. Indeed, $P(o\text{-tolyl})_3$ with a cone angle of 194° was initially believed to be unreactive although later work by Zhang and Brown found that the rate was measurable. At low (< 20 mM) concentrations of $P(o\text{-to1yl})_3$ non-pseudo-first-order kinetics were observed as a result of competition by CO recombination [50]. The reactions of **VI** with phosphites was also examined and these reagents were found to behave in much the same manner as phosphines [51]. Bursten et al. [52] expanded these kinetic studies to alkynes and established that **VI** is the reactive intermediate responsible for the formation of alkyne derivatives. Activation parameters were determined for the reactions of **VI** with a variety of ligands. Energies of activation were found to be sensitive to steric factors, while low enthalpies of activation have been interpreted by Zhang and Brown to imply a low barrier to opening of the bridging structure either in a pre-equilibrium preceding ligand binding or a concerted associative displacement [50].

The photochemical reaction of **I** with $HSnBu_3$ under flash or continuous photochemical conditions results in the formation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$, $(\eta^5\text{-}C_5H_5)Fe(CO)_2SnBu_3$ and $(\eta^5\text{-}C_5H_5)Fe(CO)(H)(SnBu_3)_2$. The suppression of this reaction by CO led Zhang and Brown [53] to conclude that the tin hydride reacts with **VI** rather than with radicals. The resulting intermediate, $(\eta^5\text{-}C_5H_5)(CO)_2Fe_2(H)(SnBu_3)(CO)(\eta^5\text{-}C_5H_5)$, which may be directly observed by IR, undergoes reductive elimination over several minutes to yield $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ and the 16 electron species $(\eta^5\text{-}C_5H_5)Fe(CO)SnBu_3$ that may react with CO or a second $HSnBu_3$ to give $(\eta^5\text{-}C_5H_5)Fe(CO)_2SnBu_3$ or $(\eta^5\text{-}C_5H_5)Fe(CO)(H)(SnBu_3)_2$, respectively. A very similar mechanism has been observed for reaction of $HSnBu_3$ with $Mn_2(CO)_{10}$ [54] and an analogous reductive elimination step is proposed in the formation of 'twist' products from ring coupled derivatives of **II** (vide infra).

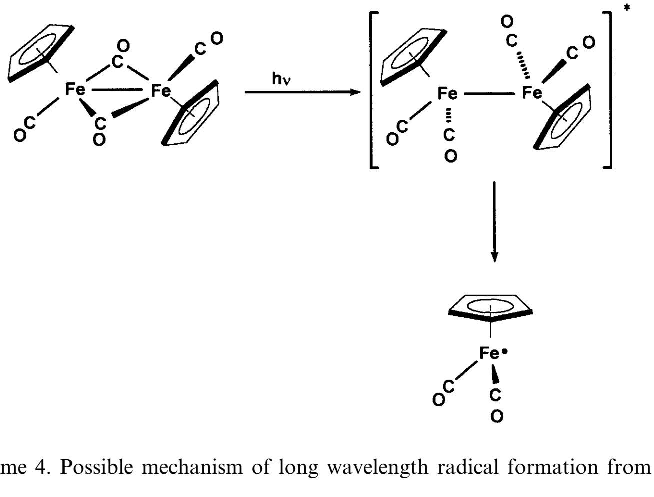
The reactions of $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ radicals with phosphites and phosphines have been studied in detail. The reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2$with $P(OCH_3)_3$ in cyclohexane at r.t. to form $(\eta^5\text{-}C_5H_5)Fe(CO)[P(OCH_3)_3]$ was found to be complete in 500 ns and was first order in both radical and ligand [55]. The rate of reaction was found to be about one order of magnitude less than the diffusion controlled limit. No evidence for the formation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[P(OCH_3)_3]$ could be observed on the time scale (ns) of these studies. Time resolved r.t. studies have found little evidence for reactions between alkyl and aryl phosphines and the $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ radicals. Such reactions are apparently slower than the rate of dimerization of the radicals. The $(\eta^5\text{-}C_5H_5)Fe(CO)[P(OCH_3)_3]$ radicals rapidly dimerize to from $(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-}CO)_2[P(OCH_3)_3]_2$ that has a bridging carbonyl stretching band at 1720 cm^{-1}. Evidence presented by Turner et al. [49,51] and Zhang and Brown [56] strongly suggest that the $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\mu\text{-}CO)(CO)LFe(\eta^5\text{-}C_5H_5)$ intermediates proposed by Gray et al. [43] are actually thermally unstable dimers of the general form $(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-}CO)_2L_2$.

In addition to reactions with halocarbons, radical cross coupling reactions have yielded heterobimetallic derivatives $(\eta^5\text{-}C_5H_5)(CO)_2FeM(CO)_3(\eta^5\text{-}C_5H_5)$, where $M = Mo$ and W [57]. Photolyses of **I** and **IV** in the presence of radical traps have yielded stable radicals that have been studied by EPR [58]. Photolyses of **I** in the presence of O_2 results in the formation of a species believed to be a peroxo complex based on its EPR signal.

A time-resolved IR study of the UV flash photolysis of *trans*, bridged **IV** established that both **VII** and the radical, $(\eta^5\text{-}C_5H_5)Fe(CO)_2$, are formed by the flash and that the radical undergoes second order recombination at close to the diffusion controlled limit to form both *cis* and *trans* **IV** in roughly equal amounts [51]. The thermally unstable *cis* isomer undergoes first order decay to the *trans* with an activation energy of 68 ± 5 kJ mol^{-1}. This surprisingly large activation energy results in the *cis* isomer having a lifetime of 40 min at $-67°C$ and ~ 50 days at $-100°C$. It is presumed that $(\eta^5\text{-}C_5H_5)Fe(CO_2)$ radicals also recombine to give *cis* and *trans* **I**, but that this effect is masked in time resolved studies by the rapid equilibrium between these two forms in solution.

Using time-resolved IR methods the branching ratio between bond homolysis and CO-loss for **I** was measured directly in cyclohexane to be $1.8 \pm 0.2:1$ at $\lambda_{irr} = 308$ nm [51]. Photolysis at $\lambda_{irr} = 510$ nm showed only homolytic cleavage, but matrix studies with $\lambda_{irr} > 475$ nm did result in the formation of trace amounts of the CO-loss product. Photolysis into the weak $d_{nb} \rightarrow \sigma^*$ transitions of *trans*, bridged **I** has the effect of breaking the Fe–Fe bond while photolysis into the $\sigma \rightarrow \sigma^*$ transition results in CO-loss. George and co-workers [59] have observed that UV irradiation and indeed visible irradiation provides energy in excess of that needed for bond breaking. For example, 308 and 510 nm photons correspond to 32 400 and 19 600 cm^{-1}, respectively, while the energy needed to break an Fe–CO bond is on the order of 30–55 kcal mol^{-1} or 11 000–20 200 cm^{-1}. Opening a bridging carbonyl to a terminal carbonyl is expected to require somewhat less energy than fully dissociating a CO. Recalling that matrix studies have established that long wavelength ($\lambda_{irr} > 475$ nm) irradiation of *trans*, bridged **I** results in bridge opening to the all-terminal form, it is possible that this process is the principal photoprocess at visible wavelengths and that homolysis is a secondary, but still fast, event arising from the vibrational excitation of this all-terminal species. This mechanism is illustrated in Scheme 4.

Femto- and picosecond studies ($\lambda_{irr} = 580$ nm) by Hochstrasser et al. [60] established that bands of both the *cis* and *trans* isomers of **I** were bleached to give new features in the terminal carbonyl region that evolved over 100 ps to bands characteristic of the (η^5-C_5H_5)$Fe(CO)_2$ radical. It is proposed that absorption of a photon generates an excited state species that rapidly gives rise to species with either one or both of the bridging carbonyl groups having been opened. These species do not appear to dissociate further to produce radicals during the first 5 ps. George and his co-workers [59] have confirmed these observations. Photolysis



Scheme 4. Possible mechanism of long wavelength radical formation from **I**.

($\lambda_{irr} = 578$ nm) of samples of **I** in cyclohexane at r.t. result in both *cis* and *trans* isomers being bleached, but monitoring of the reaction at picosecond resolution revealed only the appearance of bands associated with the $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ radical. The rapid recovery of the *cis* isomer was attributed to either recovery from an excited state of the *cis* isomer, or nonequilibrium formation of the *cis* isomer upon germinate recombination of the radicals.

Photolysis studies reported by George et al. [59] of **I** in hexane at r.t. ($\lambda_{irr} = 289$ nm) with monitoring at picosecond resolution reveals that a broad absorption band at 1830 cm^{-1} is produced by 10 ps which narrows over time to a well resolved band at 1824 cm^{-1}. The narrowing is attributed to cooling of the vibrational modes. The 1824 cm^{-1} band is identical to that of **VI** observed in matrices. A feature visible at 1908 cm^{-1} is attributed to a second transient species. Since this band has not decayed appreciably over the 70 ps time frame when the triply bridged species is fully formed it cannot be an intermediate for the triply bridged species. George has suggested that this new species may be $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)$ with a bridging carbonyl band below the 1780 cm^{-1} cutoff of the instrument. An equally valid assignment would be $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}\eta^1,\eta^2\text{-}CO)$ in which a four-electron donating bridging carbonyl would be expected to impart considerable stabilization. Other reasons for this alternate assignment will be described below.

In the presence of THF the band at 1908 cm^{-1} is not observed, but rather a band at 1945 cm^{-1}, characteristic of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\mu\text{-}CO)(THF)Fe(\eta^5\text{-}C_5H_5)$, is observed. There is no evidence of radical involvement in the formation of the THF complex, nor is **VI** a precursor. Indeed, the presence of THF reduces the extent of formation of **VI** with concurrent formation of the THF complex. Although George suggests that the THF is reacting with the 1908 cm^{-1} species, it is equally likely that it is reacting with a common precursor to the 1908 cm^{-1} species and **VI**.

Further complicating matters, Perutz et al. [61] have reported an almost identical r.t. photolysis ($\lambda_{irr} = 302$ nm) study in cyclohexane at picosecond resolution using UV–vis detection. In this work deconvolution of spectral data revealed the existence of two intermediates, A and B, that appear to be precursors of **VI** by an **A** → **B** → **VI** cascade. The lifetimes of these transient species were 1.6 ± 0.1 and 15 ± 1 ps, respectively. The very short lived species, **A**, is assigned to an excited state of *trans*, bridged **I** that undergoes CO loss to form **B** which is suggested to be *trans*-$(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-}CO)_2(CO)$. It was noted that the CO-loss species is formed as a singlet and must undergo a spin state change as well as significant molecular reorganization to form **VI**.

Although the time window of the George and Perutz experiments overlap there is no evidence in the IR studies of a transient species at less than 20 ps although the 'broad' feature that gives rise to the band at 1824 cm^{-1} may be partially associated with *trans*-$(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-}CO)_2(CO)$. No new bands in the terminal region can be discerned in the published data during this time period. The longer lived species observed by George may be a second daughter of *trans*-$(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-}CO)_2(CO)$ corresponding to a rearrangement to a second singlet species rather than undergoing spin state changes.

Moving to longer time domains further increases the number of species observed in these solutions. Zhang and Brown [53] noted that r.t. hexane solutions containing **VI** formed by xenon lamp flash photolysis did not return to baseline levels within 8 s after the flash although **VI** had completely disappeared. Upon inspection they found new bands at 1839, 1786 and 1674 cm^{-1} that decay over 2–3 h. This combination of bands and in particular the low energy band characteristic of a four-electron bridging carbonyl, suggested assignment of this species to an isomer of the triply bridged intermediate, $(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-}CO)_2(\mu\text{-}\eta^1,\eta^2\text{-}CO)$. Although this intermediate cannot be produced by visible irradiation of **I**, its decay is accelerated by visible light. Low temperature kinetic studies appear to rule out the possibility that this new species is formed directly from **VI**. Although the authors have proposed a radical pathway for formation of this new species, there is no evidence in the time-resolved studies for the formation of such a species over times during which the radicals have completely disappeared. It would be quite reasonable, however, for the species observed by these workers to arise from rearrangement of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)$ [or $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}\eta^1,\eta^2\text{-}CO)$] that George has shown to co-exist with **VI** shortly after photolysis. Scheme 5 presents a proposed mechanism that appears to account for the available data.

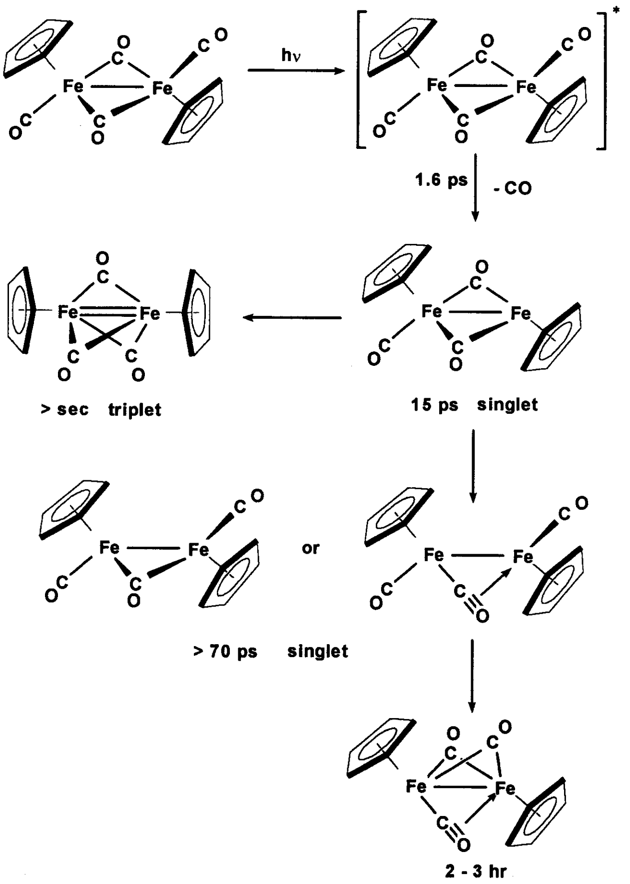
Kvietok and Bursten [62] have reported that extended UV photolysis of **I** in 3-methylpentane matrices at 98 K gives rise to **VI** as well as to new bands at 1904 and 1958 cm^{-1} which grow at the expense of **VI**. When irradiation is discontinued the bands of the new species and those of free CO decrease while bands of **VI** grow indicating that thermal back reaction is occurring even in the frozen matrix. The authors proposed that the new species is $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2$ with a formal and unsupported, Fe–Fe triple bond. Equal intensities of the two carbonyl bands require that the two carbonyl groups be orthogonal with an overall C_2 symmetry. Fensky–Hall calculations support the proposed structure.

In an effort to provide additional insight into this structure, density functional calculations have been carried out [63]. It was found that calculated structures of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2$ are very sensitive to the spin state of the species. Triplet, ^3B, $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2$ has the C_2 symmetry required by experiment, but the singlet species has C_2, symmetry with two bridging carbonyl groups.

Extended photolysis of **IV** was found to give rise to both **VII** and $[\eta^5\text{-}C_5(CH_3)_5]_2Fe_2(CO)$ as well as to a new species $[\eta^5\text{-}C_5(CH_3)_5]_2Fe_2(\mu\text{-}CO)_2$. Upon standing in the dark, the triplet species, $[\eta^5\text{-}C_5(CH_3)_5]_2Fe_2(CO)_2$, undergoes reaction with CO to reform the triply bridged species while the singlet species does not. Upon annealing to 163 K both dicarbonyl species recapture CO to form the triply bridged species. These processes are summarized in Scheme 6.

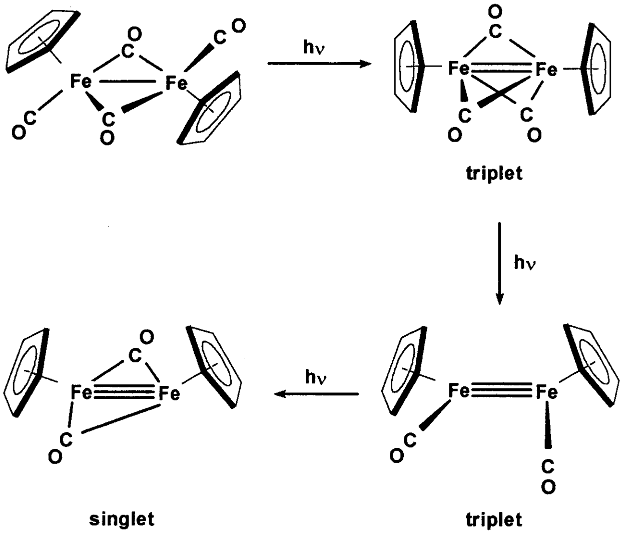
3.2. Matrix and solution studies in the presence of CO and phosphines

Photolysis of **I** under ^{13}CO or fully labeled **I** under ^{12}CO, established that the rate of CO exchange by the radical intermediate is faster than the rate of radical



Scheme 5. Proposed overall mechanism for CO-loss processes of **I**.

recombination [64]. Bloyce [65] has carried out the photolysis of **I** and **II** in frozen CO matrices at 12 K and assigned bands at 2036, 1964 and 1952 cm^{-1} to (η^4-C_5H_5)Fe(CO)$_3$ and bands at 2038, 1962 and 1950 cm^{-1} to (η^4-C_5H_5)Ru(CO)$_3$ assuming the radical to be ring based. An equally valid assignment would be (η^3-C_5H_5)M(CO)$_3$ in which the radical is metal based. Indeed, Wrighton and co-workers [66] found that photolysis of (η^5-C_9H_7)$_2$Fe$_2$(CO)$_4$ in methylcyclohexane at r.t. under an atmosphere of CO gives a short-lived species with IR bands at 2038, 1970 and 1962 cm^{-1} and an EPR singlet consistent with the formulation of the species as the 17 electron radical, (η^3-C_9H_7)Fe(CO)$_3$. An analogous triphenyl phosphine derivative was observed when the photolysis was carried out in the presence of that ligand. We have recently established that the (η^3-C_9H_7)Fe(CO)$_3$ species is very long lived at r.t. in petroleum ether under 500 psi of CO. (η^3-C_5H_5)Fe(CO)$_3$ could not be observed even at −30°C and 500 psi of CO [67]. These



Scheme 6. Extended photolysis of **I** and **IV** in frozen matrices [62,63].

η^3 species are analogous to the (η^3-C_3H_5)Fe(CO)$_3$ radical that exists in equilibrium with (η^3-C_3H_7)$Fe_2(CO)_6$ [68].

Zhang and Brown have carried out low temperature UV flash photolyses of hydrocarbon solutions of **I** under CO. At −70°C a set of bands at 2040, 1992, 1974, 1967 and 1941 cm^{-1} were observed that slowly transform into a second set of bands at 1990, 1956, 1941 and 1684 cm^{-1}. For the purposes of the following discussion these species will be designated **A** and **B**. When the photolysis is carried out at −25°C only **B** is observed. A trace of **B** may also be observed when **I** is photolyzed at −25°C under Ar. We have observed **B** at −30°C and 500 psi of CO in petroleum ether, but the lifetime of **B** under these conditions was less than 3 min. Turner has noted observing bands of a secondary product at 1977 and 1942 cm^{-1} in TRIR experiments under an atmosphere of CO. These bands appeared 'well after the end of the UV flash', but no other details are available [51].

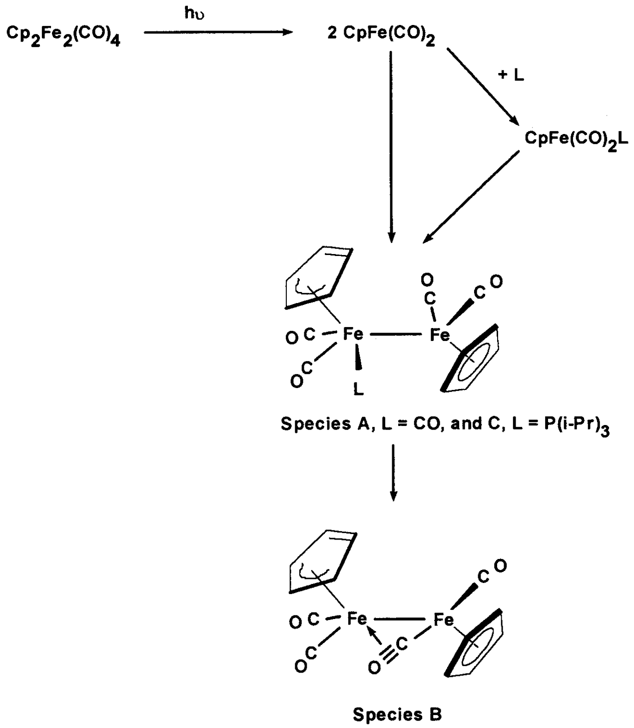
Zhang and Brown [53] have also carried out UV flash photochemical studies of **I** with P(*i*-Pr)$_3$ in 3-methylpentane at −70°C. Examining spectra 1 and 50 min after the flash revealed the presence of (η^5-C_5H_5)$_2Fe_2(CO)_3$[P(*i*-Pr)$_3$] and a second species, **C**, with IR bands at 1984, 1962, 1927 and 1911 cm^{-1} and an electronic absorption at 410 nm. This second species slowly decays over time to produce (η^5-C_5H_5)$_2Fe_2(CO)_3$[P(*i*-Pr)3] and **I**.

Zhang and Brown have proposed that the low temperature reactions of **I** with CO and P(*i*-Pr)$_3$ proceed through reaction of the(η^5-C_5H_5)Fe(CO)$_2$ radical to form (η^3-C_5H_5)Fe(CO)$_3$ and (η^3-C_5H_5)Fe[P(*i*-Pr)$_3$](CO)$_2$, respectively. These intermediates are presumed to react with a second (η^5-C_5H_5)Fe(CO)$_2$ radical to yield (η^3-C_5H_5)(CO)$_3Fe_2(CO)_2$(η^5-C_5H_5) (**A**) and (η^3-C_5H_5)(CO)$_2$[P(*i*-Pr)$_3$]$Fe_2(CO)_2$(η^5-

C_5H_5) (**C**). The authors propose that (η^3-C_5H_5)(CO)$_3$Fe$_2$(CO)$_2$(η^5-C_5H_5) undergoes CO loss to give (η^3-C_5H_5)(CO)$_2$Fe(μ-η^1,η^2-CO)Fe(CO)$_2$(η^5-C_5H_5) (**B**), which, in turn, rearranges to **I** over time. The appearance of **B** when **I** is photolyzed under Ar was attributed to heterolytic fragmentation of **I** to yield (η^5-C_5H_5)Fe(CO)$_3$ and (η^5-C_5H_5)Fe(CO). These various pathways are presented in Scheme 7.

The spectral data reported by Zhang and Brown are unusually fine, especially considering the very limited solubility of **I** in hydrocarbons at −70°C and there is no question that new species are formed at low temperature that are not observed at r.t. However, several lines of evidence suggest a somewhat more conventional alternative interpretation.

Blaha and Wrighton have reported that UV photolysis of (η^5-C_5R_5)Fe(CO)$_2$-$CH_2C_6H_5$, where R = H or CH_3, in hexane under 2 atm of CO yields *exo*-(η^4-$C_5R_5CH_2C_6H_5$)Fe(CO)$_3$ [69]. A similar reaction in the presence of PPh_3 yields *exo*-(η^4-$C_5R_5CH_2C_6H_5$)Fe(CO)$_2$(PPh_3). Even in the absence of CO, traces of the benzyl ring addition product were observed. Crossover experiments established that these reactions proceed by radical routes. The IR band positions of these compounds, species **A**, **B** and **C** and other relevant species are summarized in Table 5. Blaha and Wrighton suggest that the formation of the (η^4-C_5R_5R')Fe(CO)$_3$ species is a result of the 'extraordinary tendency of Fe(CO)$_4$ to bind dienes'.



Scheme 7. Zhang and Brown proposed a mechanism and species identities for low temperature photolysis of **I** under CO [64].

Table 5
IR carbonyl stretching frequencies of low temperature photolysis products of **I** under CO atmosphere and relevant compounds[a]

Compound	Carbonyl bands (cm^{-1})	Solvent (temp.)	Ref.
Species **A**	2040, 1992, 1974, 1967, 1941	9:1 MCH–MP (−50°C)	[64]
Species **B**	1990, 1956, 1941 (w), 1684 (w)	9:1 MCH–MP (−50°C)	[64]
Species **C**	1984, 1962, 1927, 1911	9:1 MCH–MP (−50°C)	[64]
$(\eta^3\text{-}C_3H_5)_2Fe_2(CO)_6$	2015, 1969	Petroleum ether (r.t.)	[68]
$(\eta^3\text{-}C_3H_5)Fe(CO)_3$	2046, 1968, 1060	Petroleum ether (r.t.)	[68]
$(\eta^3\text{-}C_9H_7)Fe(CO)_3$	2038, 1970, 1962	MCH (298 K)	[66]
$(\eta^4\text{-}C_5H_6)Fe(CO)_3$	2047, 1980, 1972	MCH (298 K)	[66]
$(\eta^4\text{-}C_5H_5)Fe(CO)_3$	2037, 1964, 1952	CO matrix (12 K)	[65]
trans-Nonbridged **I**	1957, 1941 (third band obscured)	Ar matrix (12 K)	[46]
$(\eta^4\text{-}C_5H_5Bz)Fe(CO)_3$	2049, 1982, 1974	MCH (r.t.)	[69]
$(\eta^4\text{-}C_5H_5Bz)\text{-}Fe(CO)_2(PPh_3)$	1977, 1924	MCH (r.t.)	[69]
$[(\eta^5\text{-}C_5H_5)(CO)_2Fe\text{–}C_5H_4]Fe(CO)_2$ $CH_2C_6H_5$	2035, 1995, 1986, 1838 (major rotamer)	pentane (r.t.)	[73]

[a] MCH = methylcyclohexane; MP = 3-methylpentane.

Baird and co-workers have reported that photolysis of $[\eta^5\text{-}C_5(CH_3)_5]Os(CO)_2\text{-}CH_2C_6H_5$ in the presence of PMe_2Ph yields $[\eta^5\text{-}C_5(CH_3)_5(CH_2C_6H_5)]Os\text{-}(CO)_2(PMe_2Ph)$ by what appears to be a mechanism identical to that of the iron compounds [70]. To our knowledge, no reports have appeared describing the chemistry of the analogous ruthenium compounds.

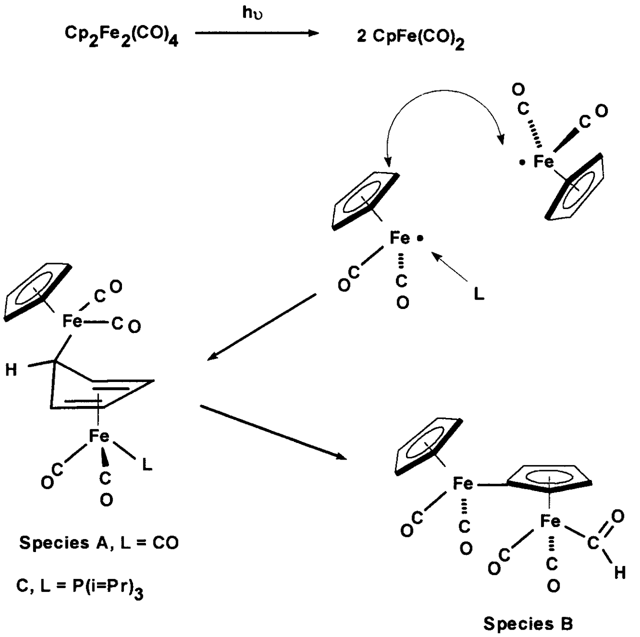
Zhang and Brown have argued that the similarity of the IR bands of species **A** with those of the $(\eta^3\text{-}C_3H_5)Fe(CO)_3$ radical, 2046, 1968 and 1960 cm^{-1}, support the assignment of **A** as $(\eta^3\text{-}C_5H_5)(CO)_3Fe\text{–}Fe(CO)_2(\eta^5\text{-}C_5H_5)$, however, the more correct analogue would have to be the Fe–Fe bonded dimer, $(\eta^3\text{-}C_3H_5)_2Fe_2(CO)_6$, that is reported to have bands at 2015 and 1969 cm^{-1}. $(\eta^4\text{-}C_5H_5R)Fe(CO)_3$ species, on the other hand, have IR bands in exactly the right regions to account for three of the bands of **A** and $(\eta^3\text{-}C_5H_5Bz)Fe(CO)_2(PPh_3)$ has IR bands in the same regions as two of the bands of **C**.

We suggest that the bands at 2040, 1974 and 1967 cm^{-1} of **A** and the bands at 1962 and 1911 cm^{-1} of **C** are associated with the $(\eta^3\text{-}C_5H_5R)Fe(CO)_2L$ units, while the bands at 1992 and 1941 cm^{-1} of **A** and 1984 and 1927 cm^{-1} of **C** are associated with a $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$ moiety. Given these assignments the IR spectral evidence for species **A** and **C** are more consistent with the structures presented in Scheme 8 in which a $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ radical has become bound to the exo face of an $(\eta^4\text{-}C_5H_5)Fe(CO)_2L$ unit. This structure was considered by

Zhang and Brown who favored the Fe–Fe bonded species on the basis of an observed UV–vis band at 392 nm associated with **A**. Further work will be necessary to resolve these interpretations.

Species **B** clearly evolves from species A over time. The IR spectrum of **B** consists of two strong and one weak bands in the terminal carbonyl region and a fourth weak band at 1684 cm^{-1}. Zhang and Brown have proposed that loss of CO by $(\eta^3\text{-}C_5H_5)(CO)_3Fe\text{–}Fe(CO)_2(\eta^5\text{-}C_5H_5)$ is accompanied by formation of $\mu\text{-}\eta^1,\eta^2\text{-}CO$ with retention of the $\eta^3\text{-}C_5H_5$ ring. The proposed species has three terminal carbonyl groups and C_1 symmetry, thus it would be expected by group theory to have three strong carbonyl stretching bands in addition to the weaker band for the four-electron bridging carbonyl group. The IR pattern of **B** consists of two strong terminal carbonyl bands at 1990 and 1956 cm^{-1} and one weak one at 1941 cm^{-1} in addition to the low energy band at 1684 cm^{-1}.

Brown, Glass and co-workers have carried out extensive studies into the formation of the formyl derivative, $(\eta^5\text{-}C_5H_5)Fe(CO)_2(CHO)$ and established by NMR that this species is formed upon low temperature (−80 to −50°C) reduction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_3]^+$ with borohydride [71]. Unfortunately, these reduction reactions were carried out in acetone because of the insolubility of $[(\eta^5\text{-}C_5H_5)Fe(CO)_3]^+$ in solvents such as THF [72] thus it was not possible to observe the IR bands of the formyl group itself. By analogy with other metal acyl groups the formyl group would be expected to have an IR band in the range 1700–1650 cm^{-1}. Upon warming of the formyl derivative, CO is lost and $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ is formed.



Scheme 8. Alternative mechanism for low temperature photolysis of **I** under CO.

Blaha and Wrighton have found that $(\eta^4\text{-}C_5H_5CH_2C_6H_5)Fe(CO)_3$ loses CO upon irradiation in frozen hydrocarbon matrices at 77 K to give $(\eta^5\text{-}C_5H_4CH_2C_6H_5)Fe(CO)_2H$ [69].

It is possible that loss of CO from species **A**, Scheme 8, allows transfer of a hydrogen yielding a hydride intermediate. Carbonyl insertion yields the formyl derivative. The overall reaction is illustrated in Scheme 8. Russian workers have carried out extensive examinations into the chemistry of so called 'stair-step' or 'ladder' compounds and have prepared $\{\eta^5\text{-}C_5H_4[Fe(\eta^5\text{-}C_5H_5)(CO)_2]\}Fe(CO)_2CH_2C_6H_5$ [73,74]. The IR bands of this compound are listed in Table 5. It is found that the $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ unit exerts an electron donating effect on the $(\eta^5\text{-}C_5H_4R)Fe(CO)_2CH_2C_6H_5$ unit and that the latter group exerts a surprisingly strong electron withdrawing effect on the former. The result is that the IR bands of the $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ group are shifted strongly up in energy. Replacing the benzyl group with a formyl group would be expected to result in even stronger electron withdrawal and shift to higher energies. As species **B** has no high energy bands in the region of 2040 cm^{-1} the model proposed for **B** in Scheme 8 cannot be correct as formulated. Further work is clearly called for to clarify the identities of these low temperature species.

3.3. Photochemistry of $(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_4$

Considerably less attention has been focused on the photochemistry of **II** and its derivatives than on **I** and, of course, nothing is known at this time about the photochemistry of **III**. The study of these compounds, particularly by time resolved IR methods and in low temperature solutions, are essential to expand our understanding of their photochemistry.

Gas matrices formed by codepositing **II** and gases such as Ar, CH_4 and N_2 onto a transmission window at 12 K were found to consist mostly of the *cis* and *trans* all terminal rotamers with only traces of the bridging form [46]. It was proposed that warming the sample to evaporate material onto the window shifted the equilibrium to an all-terminal form that was then trapped upon deposition. Photolysis of these samples at low energy ($\lambda > 375$ nm) resulted in opening of the bridged form to the *trans* terminal form with no change in the bands of the *cis* conformer. Higher energy photolysis (320 nm $< \lambda <$ 390 nm) gave rise to CO loss and a species with IR bands at 1829 cm^{-1} and an electronic absorption at $\lambda_{max} = 490$ nm. This species appears to be the ruthenium analogue of **VI**. In addition, bands at 1997 and 1928 cm^{-1} were observed and assigned to the $(\eta^5\text{-}C_5H_5)Ru(CO)_2$ radical. As noted above, photolysis of **II** in a CO matrix gave bands that were assigned to $(\eta^4\text{-}C_5H_5)Ru(CO)_3$ [65]. It appears that the matrix photochemistry of **II** parallels that of **I**. At this time no time-resolved methods have been employed to examine the photo intermediates of **II**.

Selective solution photolysis in toluene of the nonbridged form of **II** in the presence of spin traps confirmed that radical formation is the primary photoprocess and, at least under these conditions, appear to exclude CO loss as a significant process from the nonbridged isomer [75]. It was also observed that hydrogen abstraction from toluene yields $(\eta^5\text{-}C_5H_5)Ru(CO)_2H$ and that this process effectively competes with radical dimerization. Photolysis of the bridged isomer gave rise to a solvent dependent transient signal with $\lambda_{max} = 315\text{–}330$ nm assigned to $(\eta^5\text{-}C_5H_5)Ru(CO)_2\text{-}(\mu\text{-}CO)(CO)SRu(\eta^5\text{-}C_5H_5)$, where S is a solvent. An alternate assignment would be the all-terminal form, $(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_3S$.

Photolysis of **V** in benzene led to poorly defined carbonyl-free products [76]. There was no evidence of formation of carbonyl loss products analogous to those of **IV** which is surprising in light of the stability of $[\eta^5\text{-}C_5(CH_3)_5]_2Fe_2(\mu\text{-}CO)_3$.

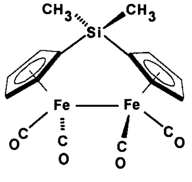
3.4. *Effect of ring coupling*

Coupling the rings of **I** and **II** forces the molecules into a *cis* orientation permitting examination of the photochemistry of this isomer. $Fe_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_5H_4CH_2C_5H_4)$ deposits in gas matrices with retention of its bridged structure. No changes in the spectrum of this material were observed with low energy photolysis, but upon high energy photolysis ($\lambda < 280$ nm) CO loss was observed with the formation of a species with three terminal carbonyl groups. $Ru_2(CO)_4(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_5H_4CH_2C_5H_4)$ (**XII**) deposits in gas matrices exclusively as the all-terminal isomer. Low energy photolysis did not result in any changes in the spectra, while high energy photolysis (320 nm $< \lambda <$ 390 nm) results in CO loss and formation of a species with three terminal carbonyl groups. The ring coupling in these cases precludes formation of triply bridged species.

Substitution of carbonyl ligands of ring-coupled iron compounds by phosphines and diphosphines appears to require photochemical conditions [77–79].

While no time resolved kinetics studies have been carried out on the ring coupled compounds, Bursten et al. [80] have carried out a competition experiment between **I** and $Fe_2(\mu\text{-}CO)_2(CO)_2[\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_5H_4Si(CH_3)_2C_5H_4]$ (**XIII**), with phenylacetylene as the reactant. Photolysis of an equimolar mixture of the two metal complexes with UV irradiation established that the two acetylene addition products were formed in a 2.10 ± 0.35 ratio. As the relative quantum yields of the two photoprocesses are not known it is not possible to compare rates of reactions of the two intermediates.

Nelson and Wright have reported that the benzyl derivative, $[Fe(CO)_2CH_2C_6H_5]_2[\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_5H_4Si(CH_3)_2C_5H_4]$ appears to have enhanced reactivity for photofragmentation relative to the mononuclear compound $(\eta^5\text{-}C_5H_5Fe(CO)_2\text{-}CH_2C_6H_5)$ [81]. UV photolysis of the binuclear benzyl derivative yields **XIII** and

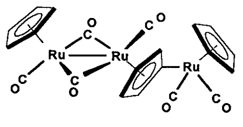


XIII

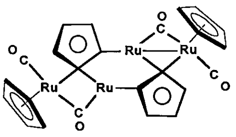
dibenzyl. Mechanistic studies established that benzyl radicals were formed in the course of the reaction and crossover experiments employing benzyl and benzyl-d_7 derivatives give the distribution of dibenzyl expected of a radical mechanism. The reaction is inhibited by PPh_3. Interestingly, dibenzyl could also be generated by reaction of Me_3NO with the binuclear compound prompting the authors to propose a mechanism involving CO loss. An analogous mechanism has been proposed by Tyler for the photofragmentation of $(\eta^5\text{-}C_5H_5)W(CO)_3CH_3$ [82].

4. Photochemical rearrangements and substitution reactions

Extended (3 day) UV photolysis of **II** in toluene has been found by Knox et al. [83] to produce reaction mixtures from which two polynuclear compounds could be isolated. Compound **XIV** is believed to be formed by radical attack at one cyclopentadienyl ring of **II**, while the putative intermediate leading to the tetranuclear species, **XV**, is proposed to be the result of radical attack on the second ring followed by CO loss. Given the very long period of photolysis it is unwise to speculate about intermediates in this process. As noted above, photolysis of **II** in toluene is now known to efficiently produce hydrides by hydrogen abstraction. NMR measurements made on briefly photolyzed solutions of **I** in benzene-d_6 are found to have Ru–H resonances as well [84], so the actual mechanism of the formation of **XV** remains obscure.



XIV

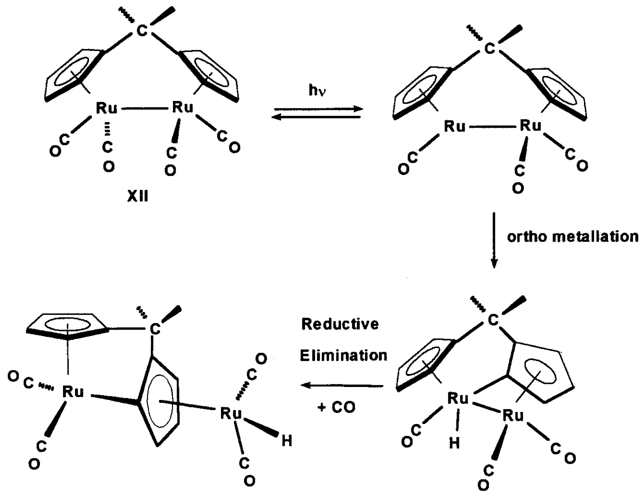


XV

Photolysis of **XII** or its two carbon analogue in solution result in the formation of unique new species in which Ru–Ru and one ring C–H bond have been broken and a Ru-ring and Ru–H bond formed. These ‘twist’ molecules can be isolated as their chlorides. Based on similarities with the analogous Mo and W compounds, it is believed that these reactions proceed by the mechanism illustrated in Scheme 9 in which a CO group is lost followed by *ortho*-metallation and ultimately rearrangement and recapture of CO [85].

The silane bridged compound, $Ru_2(\mu\text{-}CO)_2(CO)_2[\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_5H_4Si(CH_3)_2C_5H_4]$ (**XVI**) also undergoes ‘twist’ formation, but this product is itself sensitive to photolysis resulting in the formation of a fully rearranged isomer, Scheme 10. Analogous thermal rearrangements have been reported although the mechanism in these cases remains unclear [20a–c].

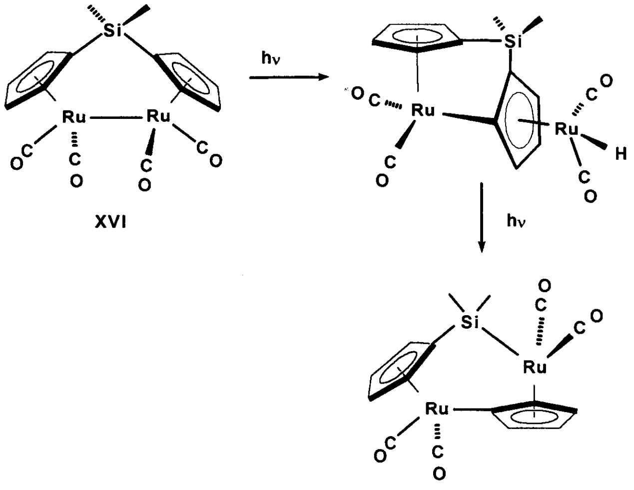
A similar reaction has been observed by Vollhardt and Weidman [86] upon visible photolysis of the fulvalene derivative, $Ru_2(CO)_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_5H_4C_5H_4)$ (**XVII**), to yield a species in which the Ru–Ru and Cp–Cp bonds have been broken and exchanged (Scheme 11). The reaction is reported to be insensitive to the presence of



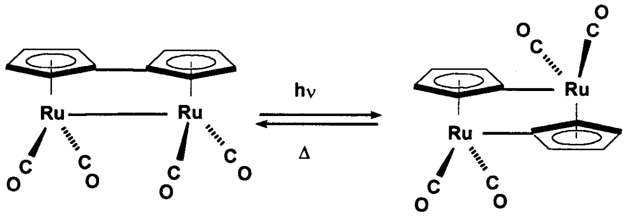
Scheme 9. Proposed mechanism of the 'twist' reaction of ring-coupled ruthenium derivatives.

either CO or THF, thus seemingly ruling out a CO– loss process. The reaction can be reversed thermally giving an elegant example of a molecular light energy storage device [87].

As noted in the introduction, the initial applications of photochemistry to the Group VIII bimetallic compounds were for the purpose of carrying out ligand exchange reactions that were either impossible under reflux conditions, or that led to thermally unstable products. Both thermal and photochemical processes can thus be used for substitution of one or two carbonyl groups by other ligands.



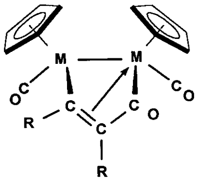
Scheme 10. Photochemical 'twist' reaction of **XVI**.



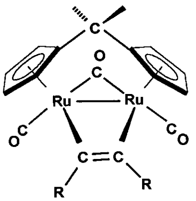
XVII

Scheme 11. Photochemical isomerization of **XVII** [86].

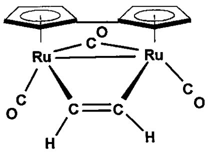
Photolysis of either **I** or **II** with acetylenes gives rise to products **XVIII**, in which one of the metal carbonyl groups has been incorporated into a fluxional dimetallacyclopentenone ring [88]. A similar product is formed by ring coupled iron derivatives, but **XII** [79,89] and **XVII** [90] give products in which the acetylene is μ-η^1-η^1 (or parallel) bridging between the two metals, **XIX** and **XX**. An extensive chemistry for $(\eta^5\text{-}C_5H_5)_2Ru_2(CO)(\mu\text{-}CO)[\mu\text{-}C(O)PhC_2Ph]$ involving acetylene exchange with other ligands such as trimethylphosphite, ethene and allene has been reported [91]. Photolysis of **XII** with PPh_3 yields **XXI** as the only product which appears to be a secondary photolysis product of the expected $Ru_2(CO)_2(PPh_3)(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_5H_4CH_2C_5H_4)$ species in which a second carbonyl group has been lost and the electron deficient metal has inserted into a P–Ph bond. No evidence for the simple



XVIII

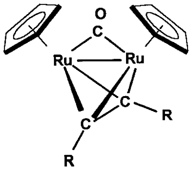


XIX

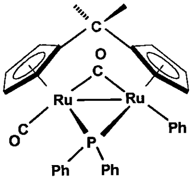


XX

phosphine substitution product has been observed suggesting that photolysis of this species proceeds with a higher efficiency than that of the starting ruthenium compound [77].


XXI

Photolysis of (η^5-C_5H_5)$_2$$Ru_2$(CO)($\mu$-CO)[$\mu$-C(O)Ph$C_2$Ph] yields a remarkably stable double CO loss product (η^5-C_5H_5)$_2$$Ru_2$($\mu$-CO)[$\mu$-$\eta^{2:2}$-Ph$C_2$Ph] (**XXII**), which has a rich chemistry [92]. The single CO loss intermediate in this process has not yet been observed.

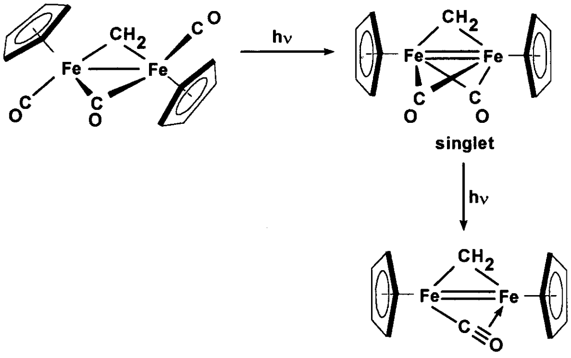

XXII

5. Photochemistry of μ-CHR bridged dimers

The synthetic chemistry of the family of alkylidene complexes (η^5-C_5H_5)$_2$$M_2(CO)_2$($\mu$-CO)($\mu$-CHR), where M = Fe [93] and Ru [94], compounds is well developed and excellent routes to these compounds are available. Under irradiation it has been found that these compounds add one or more acetylenes to build chains [95] Photolysis of (η^5-C_5H_5)$_2$$Ru_2(CO)_2$($\mu$-CO)($\mu$-$CH_2$) with ($Ph_2P$)$_2$$CH_2$ yields (η^5-C_5H_5)$_2$$Ru_2$[$\mu$-($Ph_2P$)$_2$$CH_2$]($\mu$-CO)($\mu$-$CH_2$) [96].

As noted earlier, Bursten and his co-workers have used Fenske–Hall molecular orbital calculations to model the series of iron dimers, (η^5-C_5H_5)$_2$$Fe_2(CO)_2$($\mu$-CO)($\mu$-L), where L = CO, CH_2, C=CH_2 and CH^+ [30]. The molecular orbital diagrams of **I** and (η^5- C_5H_5)$_2$$Fe_2(CO)_2$($\mu$-CO)($\mu$-$CH_2$) are presented in Scheme 3. Recognizing the similarities between the alkylidene bridged compounds and **I**, McKee and Bursten [97] examined the photochemistry of (η^5-C_5H_5)$_2$$Fe_2(CO)_2$($\mu$-CO)($\mu$-$CHCH_3$)

UV irradiation of (η^5-C_5H_5)$_2$$Fe_2(CO)_2$($\mu$-CO)($\mu$-$CHCH_3$) in toluene doped with CCl_4 resulted in formation of (η^5-C_5H_5)Fe(CO)$_2$Cl, but no evidence for (η^5-C_5H_5)Fe(CO)($CHCH_3$)Cl expected from a (η^5-C_5H_5)Fe(CO)(μ-$CHCH_3$) radical could be found. Crossover experiments involving $Mn_2(CO)_{10}$ and **IV** also failed to yield evidence for photochemical homolysis.



Scheme 12. Matrix photochemistry of *trans*-$[\eta^5\text{-}C_5(CH_3)_5]_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ [97].

Flash photolysis studies of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ established the existence of a species with an absorbance at $\lambda_{max} = 485$ nm and a weaker absorbance at 625 nm that was proposed to be the CO-loss intermediate $(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-}CO)_2(\mu\text{-}CHCH_3)$. This intermediate was found to react with phosphines and phosphites, but not THF to yield the expected substitution products $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)(\mu\text{-}CO)L(\mu\text{-}CHCH_3)$. Enthalpies of activation for the phosphine addition reactions are slightly lower than those observed for analogous additions to **VI** and this difference is attributed to the absence of spin state changes in the alkylidene intermediate as opposed to the triply carbonyl bridged intermediate.

Efforts to examine the matrix photochemistry of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ were complicated by the presence of multiple isomers and low solubility, but the photolysis of *trans*-$[\eta^5\text{-}C_5(CH_3)_5]_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ was successfully carried out [98]. Broad band UV photolysis was found to cleanly give rise to a CO-loss species, $[\eta^5\text{-}C_5(CH_3)_5]_2Fe_2(\mu\text{-}CO)_2(\mu\text{-}CH_2)$ which subsequently loses CO to form $[\eta^5\text{-}C_5(CH_3)_5]_2Fe_2(\mu\text{-}\eta^1,\eta^2\text{-}CO)(\mu\text{-}CH_2)$, Scheme 12. The relationship between the double CO-loss species and the single CO-loss species was confirmed by following the thermal back reaction of CO.

6. Conclusions

The photochemistry of the Group VIII cyclopentadienyl, carbonyl bimetallic compounds is well developed as a versatile synthetic tool and the current level of understanding of the mechanisms and intermediates involved in this chemistry is extensive if not complete. Detailed mechanistic studies have made it possible to eliminate certain proposed mechanisms, but the plethora of intermediates that have been reported leave fertile ground for future investigations. The mechanistic chemistry of the ruthenium and especially the osmium compounds is still largely unexplored and would greatly benefit from the application of modern time-resolved methods. To put these issues in a broader perspective, it is important to recognize that the photochemistry of this class of compounds is one of the most examined and best understood which only serves to underscore our broad ignorance of organometallic photochemistry. It is unlikely that the photochemical community will have difficulties identifying interesting and relevant problems well into the next millennium.

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