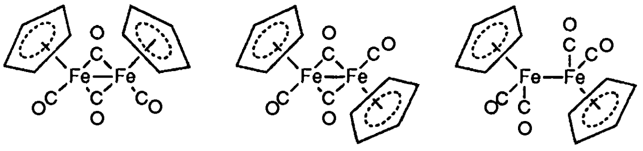
Photochemistry of Some Iron and Ruthenium (η^5-Cyclopentadienyl) Carbonyl Dimers in Frozen Gas Matrices at *ca.* 12 K†

Peter E. Bloyce, Andrew K. Campen, Richard H. Hooker, Antony J. Rest,* and Neil R. Thomas
Department of Chemistry, The University, Southampton SO9 5NH
Thomas E. Bitterwolf
Department of Chemistry, College of Letters and Sciences, University of Idaho, Moscow, Idaho 83843, U.S.A.
Joyce E. Shade
Department of Chemistry, United States Naval Academy, Annapolis, Maryland 21402, U.S.A.

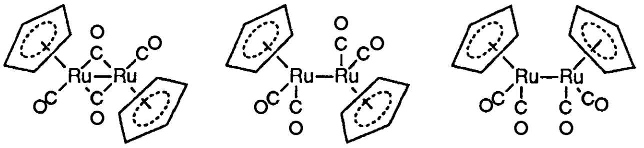
The photochemistry of $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ [M = Fe, (**1**); or Ru, (**2**)] and $[CH_2\{(\eta^5\text{-}C_5H_4)M(CO)_2\}_2]$ [M = Fe, (**5**); or Ru, (**6**)] has been studied in frozen-gas matrices (Ar, CH_4, and N_2) at *ca.* 12 K and that of (**2**) in poly(vinyl chloride) (pvc) films at *ca.* 12 K. Low-energy photolysis of compounds (**1**) and (**2**) was found to induce opening of *trans*-carbonyl-bridged species affording terminal carbonyl species. Photolyses into the electronic absorption band maxima of these new terminal-carbonyl species yielded 17-electron radical species $[M(\eta^5\text{-}C_5H_5)(CO)_2]^{\cdot}$ as well as small amounts of triply carbonyl-bridged species, $[M_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)_3]$. At the corresponding maxima of *trans*-carbonyl-bridged complexes (**1**) and (**2**) photolysis yielded the triply-carbonyl-bridged species directly. Photolysis of (**5**), which is exclusively bridging and is constrained by the methylene linkage between the rings to be in a *cis* conformation, at a range of wavelengths showed no evidence for carbonyl-bridge opening. At its electronic absorption maxima photolysis resulted in carbonyl ejection and formation of a new species whose spectrum is consistent with its having three terminal carbonyl groups and an Fe–Fe double bond. Photolysis of compound (**6**) which exists in a *cis*-terminal conformation also resulted in carbonyl loss and formation of a species similar to that observed for (**5**). These results are discussed in terms of their relationship to previous photochemical studies of (**1**) and (**2**) and an overall model for the photochemical behaviour of (**1**) and (**2**) is presented.

There are a number of structurally well characterised dinuclear organometallic complexes which have direct metal–metal bonds or their equivalent such as in the case of $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ (1) in which the $Fe_2(CO)_2$ core exhibits delocalised bonding behaviour.[1] The photochemistry of many of these compounds has been investigated.[2] Photoexcitation of these compounds is generally proposed to proceed *via* metal-centred radicals[2] although alternative pathways involving ligand ejection have also been observed.[3] Several detailed photochemical studies of compounds (1) and $[Ru_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ (2) have been carried out which suggest that both radical and non-radical intermediates may be formed upon photolysis.

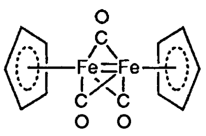
Caspar and Meyer[4] found that two distinct species could be detected by u.v. spectroscopy after flash photolysis of solutions of (1). Turner and co-workers[5] have conducted similar experiments incorporating high-speed i.r. spectroscopy which permitted the two species to be identified as the cyclopentadienyliron dicarbonyl 17-electron radical, $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^{\cdot}$ (3), and a triply carbonyl-bridged species $[Fe_2(\eta^5\text{-}C_5R_5)_2(\mu\text{-}CO)_3]$ (4). Compound (4; R = H) was first independently observed in poly(vinyl chloride) (pvc) films and methane matrices at 12 K[6] and organic glasses[7] at 77 K. Wrighton and co-workers[8] have isolated (4; R = Me) and have reported a molecular structure of this compound. Interestingly this compound is paramagnetic, *i.e.* a spin triplet.[8]



(1)



(2)

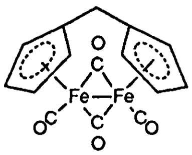


(4)

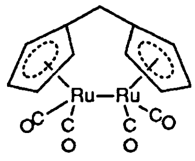
Compound (1) has been shown to undergo substitution of its carbonyl ligands by phosphines photochemically.[9] Wrighton and co-workers[10] examined the phosphite reactions of (1) and (2) in the presence of halide donors such as CCl_4 and BuI and found that only cyclopentadienylmetal dicarbonyl halide products were isolated, indicating that the photosubstitutions were proceeding through radical intermediates. Turner and co-workers[11] have examined the reactions of (1) with acetonitrile and phosphines under flash-photochemical conditions at room

---

† *Non-S.I. units employed:* Torr ≈ 133 Pa, atm = 101 325 Pa.



(5)



(6)

temperature and found that while radicals are formed in small amounts they rapidly disappeared. In contrast, the triply bridged intermediate was the dominant intermediate species in these reactions. Subsequently, very high-speed i.r. studies of the radical species formed upon flash photolysis at room temperature have shown that the radical (3) can rapidly react with phosphites to form cyclopentadienyliron carbonyl phosphite radicals.[12] There was no evidence for the existence of a 19-electron cyclopentadienyliron dicarbonyl phosphine radical which either does not form at all or loses carbon monoxide at a rate faster than that of the resolution of the experimental technique (500 ns). Most recently, the use of picosecond time-resolved i.r. spectroscropy to study the spectra and kinetics of the primary products obtained on visible photolysis of compound (1) in hexane has demonstrated that the species formed with a rise time of 50 ps, *i.e.* the initial photoproduct, has a structure in which the Fe–CO bridge bonds are broken.[13] It is significant that the primary process does not appear to be Fe–Fe bond cleavage to yield radicals, *i.e.* $[\mathrm{Fe}(\eta^5\text{-}C_5H_5)(CO)_2]^{\bullet}$.[13]

Bursten *et al.*[14] have made competition studies between compound (1) and pairs of alkynes and concluded that the observed ratios are most consistent with the CO-loss intermediate (4). These observations contradicted earlier suggestions by these workers[15] that a non-CO-loss intermediate might be involved in the alkyne reaction. Gray and co-workers[16] have examined relatively low-energy photochemical reactions of (1) with $P(OMe)_3$ in tetrahydrofuran (thf) and ethyl chloride at −78 °C and found that an intermediate is produced which contains a bridging carbonyl group but no metal–metal bond. The evidence presented indicates that this intermediate is formed by a non-radical process. Finally, in a series of papers Tyler and co-workers[17] have reported the results of mechanistic studies of the photochemical disproportionation reactions of (1). Mechanisms involving the initial production of the radical species (3) have been proposed.

The studies described above present a complex, if not seemingly contradictory, set of observations on the photochemistry of compounds (1) and (2) which are further complicated by the use of several photochemical techniques and irradiating wavelengths. In an effort to clarify the photochemical behaviour of these compounds under conditions where thermal and solvent effects were minimised a matrix-isolation study of the photochemistry of (1), (2), and their ring-coupled derivatives $[CH_2\{(\eta^5\text{-}C_5H_4)\mathrm{Fe}(CO)_2\}_2]$ (5) and $[CH_2\{(\eta^5\text{-}C_5H_4)\mathrm{Ru}(CO)_2\}_2]$ (6) has been carried out. The results of this study bear significantly on the mechanisms of photochemical reactions of (1) and (2) and provide evidence for intermediates which permit a simplified interpretation of the chemistry observed by Gray. The implications of these observations for synthetic studies are also noted.

Experimental

Compound (1) was purchased from Strem Chemicals and used as received; (2),[18] (5),[19] and (6)[19] were prepared according to literature procedures. Gas matrices were prepared at high dilution by a slow spray-on technique using conditions and gases described previously.[20] Deposition temperatures for the various dimers were: (1), 90; (2), 92; (5), 95; and (6), 100 °C. Films of pvc were cast from thf solution using a technique described in detail elsewhere.[21]

Infrared spectra (resolution about 1 cm^{-1}) were recorded on a Nicolet 7199 Fourier-transform spectrometer (number of data points = 16 364, number of transform points = 32 768). The formation of new species was monitored primarily using the terminal and bridging carbonyl stretching regions in the i.r. spectra. Electronic absorption spectra were recorded using a Perkin-Elmer Lambda-7 UV/VIS spectrometer.

The photolysis source was a Philips HPK 25-W medium-pressure mercury arc lamp and wavelength-selective photolysis was achieved using a combination of absorbing materials. The following filters were used: filter A (λ >475 nm), Corning Glass Filter no. 3385 (3 mm thick); B (λ >420 nm), Corning Glass Filter no. 3389 (3 mm thick); C (λ >375 nm), Corning Glass Filter no. 3060 (3 mm thick); D ($320 < \lambda < 390$ nm), Corning Glass Filter no. 5874 (3 mm thick); E ($290 < \lambda < 370, \lambda > 550$ nm), quartz glass cell containing Br_2 (200 Torr, pathlength 27 mm) + Pyrex disc (2 mm thick); and F (λ <280, λ >550 nm), quartz glass cell containing Cl_2 (2 atm, pathlength 27 mm) + quartz glass cell containing Br_2 (200 Torr, pathlength 27 mm).

Results

(*a*) *Photolysis of* $[\mathrm{Ru}_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$, (2), *in pvc Films at* 12 K.—We have previously shown[6] that photolysis of compound (1) in pvc films at 12 K leads to photochemical loss of CO and concurrent formation of the triply carbonyl-bridged dimer (4); the photolysis is completely reversed by subsequent warming of the film to 200 K. An identical process was observed in Nujol mulls and KBr discs at 12 K.

The i.r. spectrum of compound (2) at room temperature (298 K) in a pvc film (3 mg per 500 mg) cast from a thf solution (298 K) is shown in Figure 1(*a*). The spectrum is similar to that observed[22c] for the dimer in polar solvents. The dimer exists as *cis*- and *trans*-non-bridged isomers in equilibrium with carbonyl-bridged isomers. The bands C and T in the spectrum at 1 995, 1 955 (sh), 1 808, and 1 775 cm^{-1} are assigned to the *cis*- and *trans*-bridged isomers, whilst C′ and T′ seen at 2 010 (sh), 1965, and 1 931 cm^{-1} are assigned to the *cis*- and *trans*-non-bridged isomers, respectively, by analogy with solution spectra.[22] The electronic absorption spectrum of (2) in a pvc film at room temperature [Figure 2(*a*)] shows two bands in the near-u.v. region with maxima at 275 and 330 nm. These are assigned to $\sigma \longrightarrow \sigma^*$ (Ru–Ru) transitions in the carbonyl-bridged and non-bridged isomers, respectively, again by analogy with reported solution spectra.[22] Cooling the film to 12 K [Figures 1(*b*) and 2(*b*)] resulted in some conversion of the non-bridged isomers of the dimer into the bridged isomers. Subsequent irradiation (filter E) of the film at 12 K led to an increase in the bands for the *cis*- and *trans*-non-bridged isomers, whilst the bands for the bridged isomers decreased in intensity [Figures 1(*c*) and 2(*c*)], *i.e.* the bridged isomers undergo photoinduced 'bridge opening.' A complete reversal of the photoreaction was observed on warming the film to *ca.* 40 K [Figure 1(*d*)]. No i.r. spectroscopic evidence for the carbonyl-loss product was obtained on near-u.v. (filter D) or visible (filter B) irradiation of compound (2) in pvc films at 12—77 K.

(*b*) *Photolysis of* $[\mathrm{Ru}_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$, (2), *in Methane, Argon, and Nitrogen Matrices.*—The i.r. spectrum (CO stretching region) of compound (2) isolated at high dilution in a pure methane matrix is shown in Figure 3(*a*). This spectrum shows two strong terminal CO stretching bands at 1 974 and 1 944 cm^{-1} together with two weaker bands in the same region (2 021 and 1 964 cm^{-1}) and one weak band in the bridging CO region at 1 787 cm^{-1}. These data are summarised in Table 1. The

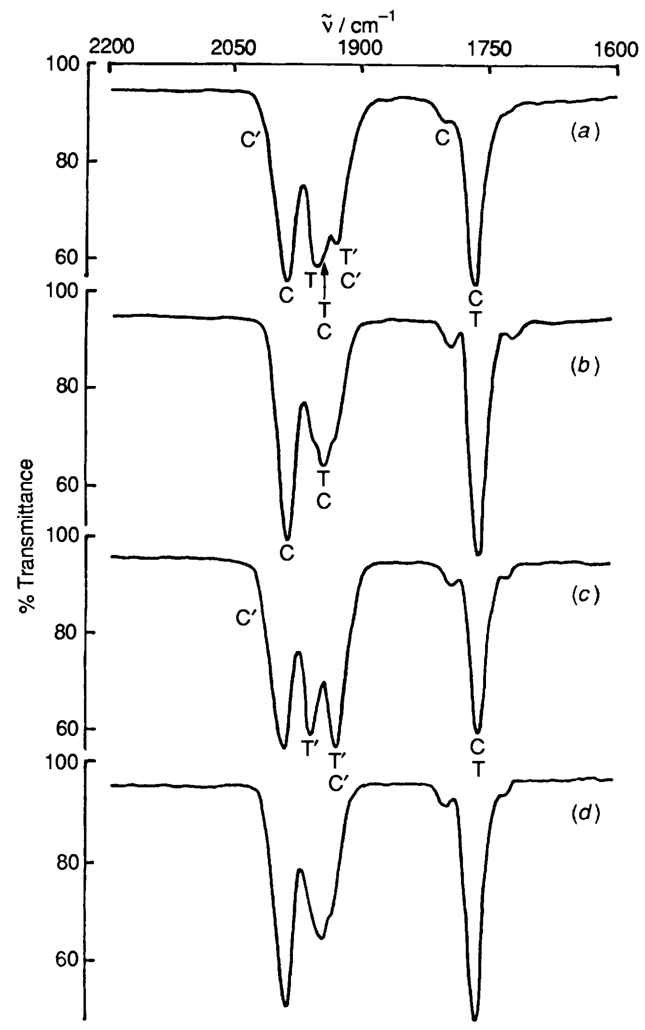


Figure 1. I.r. spectra from an experiment with $[Ru_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ in a pvc film (cast from thf solution): (*a*) at 298 K, (*b*) after cooling to 12 K, (*c*) after irradiation for 15 min ($\lambda > 300$ nm) at 12 K, and (*d*) after warming the film to *ca.* 40 K. Bands marked C and T are for *cis*- and *trans*-bridged isomers, C′ and T′ for non-bridged isomers

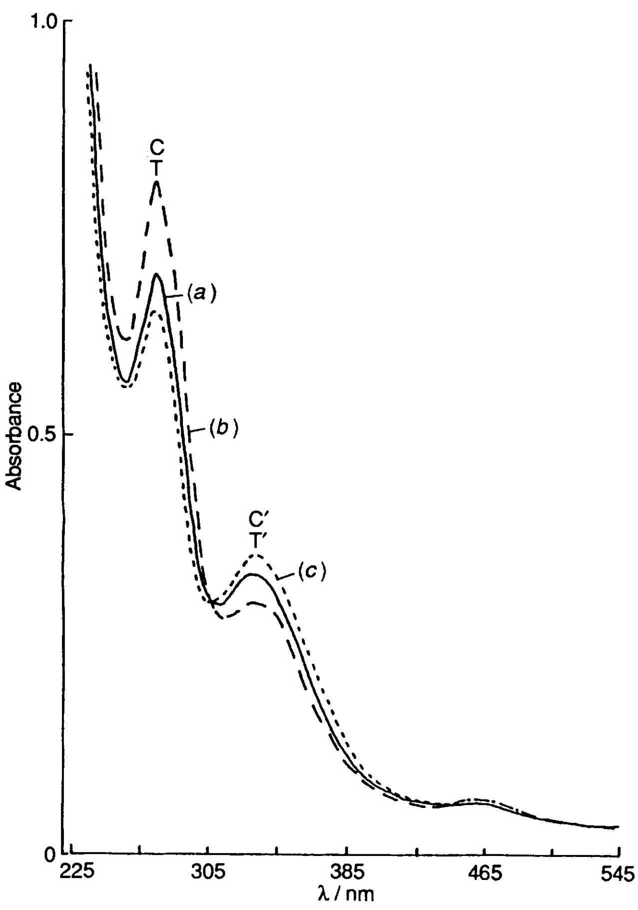


Figure 2. U.v.–visible spectra from an experiment with $[Ru_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ in a pvc film (cast from thf solution): (*a*) at 298 K, (*b*) after cooling to 12 K, and (*c*) after irradiation for 15 min ($\lambda > 300$ nm) at 12 K. Symbols as in Figure 1

spectrum can be explained by considering that in solution (**2**) can exist as an equilibrium mixture of four different conformers[22] whose relative concentrations are very dependent on both temperature and solvent polarity. By comparison with the assigned solution spectra[22] it is possible to assign the bands of the matrix-isolated sample to specific conformations. The majority of the dimer is present in the *trans*-non-bridged form (ν_{CO} 1 974 and 1 944 cm^{-1}) together with some *cis*-non-bridged isomer (ν_{CO} 2 021 and 1 944 cm^{-1}), and a little of the *trans*-bridged form (ν_{CO} 1 964 and 1 787 cm^{-1}). None of the *cis*-bridged isomer is observed. A similar spectrum was observed after deposition in all gas matrices. In the gas matrices the sample must be trapped in its preferred high-temperature (gas-phase) form, *i.e.* the non-bridged isomers,[22a] by the instantaneous temperature drop as the sample vapour and matrix gases cocondense onto the cryostat window.

Initial photolysis predominantly into the lowest-energy electronic absorption (filter C) [Table 2, Figure 4(*a*)] resulted in the disappearance of the bands for the *trans*-bridged isomer with a corresponding increase in the bands for the *trans*-non-bridged form, the bands for the *cis*-non-bridged isomer remaining constant in intensity [Figures 3(*b*) and 3(*c*)]. The photoinduced 'bridge opening' observed in pvc films is also clearly taking place in the methane matrix.

Photolysis with near-u.v. light (filter D) resulted in the production of three new bands at 1 997, 1 928, and 1 829 cm^{-1} as well as a band at 2 138 cm^{-1} [Figure 3(*d*)]. Continued photolysis at this or higher energy (filter E) did not produce any increase in the two weak bands at 1 997 and 1 928 cm^{-1}, however the band at 1 829 cm^{-1} and that for 'free' CO (2 138 cm^{-1}) continued to grow along with other extremely weak new bands at 1 915, 1 853, and 1 806 cm^{-1}, all at the expense of the parent bands of the *trans*-non-bridged conformer [Figure 3(*e*)]. As the i.r. band at 1 829 cm^{-1} was produced, a weak new band was seen to grow in the electronic absorption spectrum ($\lambda_{max.}$ = 490 nm) [Figure 4(*b*)]. After further irradiation into this u.v. band (filter A) this band and the i.r. bands at 1 829 and 2 138 cm^{-1} ('free' CO) decreased while the parent *trans*-bridged bands grew once more [Figure 3(*f*)]. Annealing the matrix to about 40 K resulted in all new bands decreasing in intensity and the parent bands of both the *trans*-bridged and non-bridged isomers growing.

In argon matrices an identical bridge opening was seen on low-energy photolysis (filter C) and, allowing for matrix shifts, one of the species seen in CH_4 was produced on near-u.v. irradiation (filter D) (ν_{CO} 2 007 and 1 931 cm^{-1}), but the other new bands observed at 1 829 and 2 138 cm^{-1} in methane were not seen in argon (Table 1). This new species seen in both argon and methane matrices is clearly not a product of carbonyl loss from the parent. No new bands were produced in the electronic absorption spectrum of the sample isolated in the argon matrix.

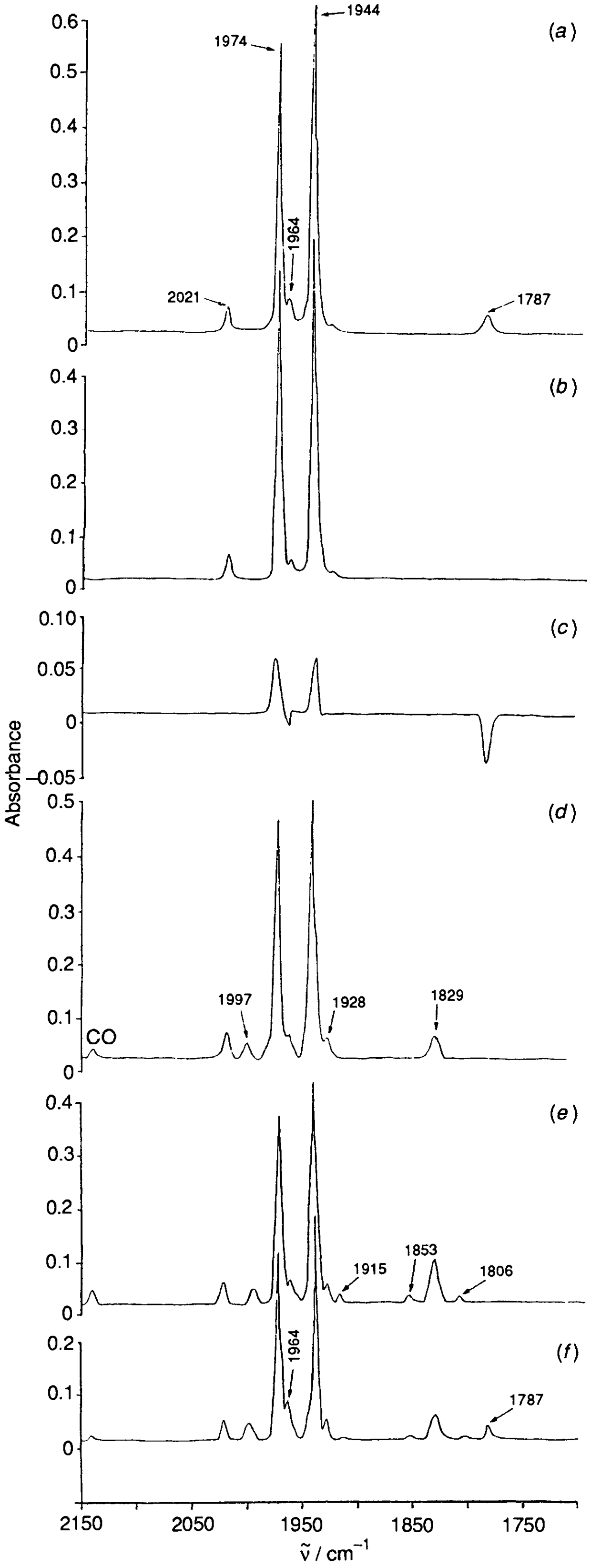


Figure 3. Infrared spectra (Nicolet 7199, resolution 1 cm^{-1}) from an experiment with [$Ru_2(\eta^5\text{-}C_5H_5)_2(CO)_4$] isolated at high dilution in a methane matrix: (*a*) after deposition, (*b*) after irradiation using filter C (60 min), (*c*) subtraction spectrum [(*b*) − (*a*)], (*d*) after irradiation using filter D (90 min), (*e*) after irradiation using filter E (30 min), and (*f*) after irradiation using filter A (90 min)

Table 1. Observed positions (cm^{-1}) of CO-stretching modes of the isomers of compounds (**1**)[a] and (**2**) and their photoproducts in argon, methane, and nitrogen frozen-gas matrices and pvc films at 12 K

Compound	Argon	Methane	Nitrogen	pvc Film
(**1**) *cis*-bridged	2 007	2 006	2 008	1 992[b]
	1 962	1 961	1 964	1 952
	1 806	1 804	1 807	1 799
	1 758	1 757	1 760	1 772
trans-bridged	1 962	1 961	1 964	1 952[b]
	1 792	1 785	1 793	1 772
trans-non-bridged	1 959	1 955	1 959	[c]
	1 941	1 936	1 941	
(**2**) *trans*-bridged[d]	1 967	1 964	1 969	1 955
	1 792	1 787	1 790	1 775
trans-non-bridged[e]	1 976	1 974	1 978	1 965
	1 946	1 944	1 947	1 931
cis-non-bridged[f]	2 023	2 021	2 025	2 010
	1 946	1 944	1 947	1 931
(**3**)[g]	1 998	1 994	2 000	[c]
	[h]	[h]	[h]	
(**4**)[i]	1 819	1 813	1 820	1 812
(**8**)	[j]	1 829	1 832	[c]
(**7**)	2 001	1 997	2 002	[c]
	1 931	1 928	1 931	

[a] ν_{CO} at 2 004, 1 958, and 1 783 cm^{-1} in CCl_4 at 298 K; at 1996, 1 952, and 1 780 cm^{-1} in benzene at 298 K.[10] [b] Data from ref. 6*b*. [c] Species not observed in experiments with pvc films.[6b] [d] ν_{CO} at 1965 and 1 794 cm^{-1} in heptane at 298 K.[22c] [e] ν_{CO} at 1 973 and 1 944 cm^{-1} in heptane at 298 K.[22c] [f] ν_{CO} at 2 020 and 1 944 cm^{-1} in heptane at 298 K;[22c] *cis*-bridged isomer observed in pvc films (ν_{CO} at 1 995, 1 955, 1 808, and 1 775 cm^{-1}).[6b] [g] ν_{CO} at 2 004 and 1 938 cm^{-1} in cyclohexane at 295 K.[5] [h] Band obscured by i.r. band of *trans*-non-bridged (**1**). [i] ν_{CO} at 1 823 cm^{-1} in cyclohexane at 295 K.[5] [j] Not observed because of band overlaps.

Table 2. Electronic absorption bands ($\lambda_{max.}$/nm) for compounds (**1**), (**2**), and (**6**) and some relevant photoproducts in CH_2Cl_2 solutions and gas matrices at 12 K

Compound	Gas matrix at 12 K[a]	CH_2Cl_2 Solution at 298 K
(**1**)	515	515
	420[b]	
	345	350
(**2**)	430	434
	335	334
	270[c]	265
(**4**)	505[d]	510[e]
(**6**)	435[f]	430
	325	330
	260[c]	260[c]
(**8**)	490[f]	
(**11**)	425	

[a] All spectra in argon matrices, except for (**2**) in methane. [b] Absorption due to non-CO-bridged isomer of (**2**). [c] Shoulder. [d] Tentative assignment, R = H. [e] Cyclohexane solution, R = Me. [f] Very weak.

In nitrogen matrices the photochemical bridge opening of the small amount of *trans*-bridged isomer present was again observed on low-energy photolysis (filter C). The photochemistry was then observed to follow an identical pattern as in the methane matrix, with no evidence for any dinitrogen co-ordination in the photoproducts or any other new bands not observed in CH_4 (Table 1).

Two species are apparently produced on near-u.v. irradiation of the *trans*-non-bridged isomer. From the argon experiment it is clear that the species with CO stretching frequencies at about

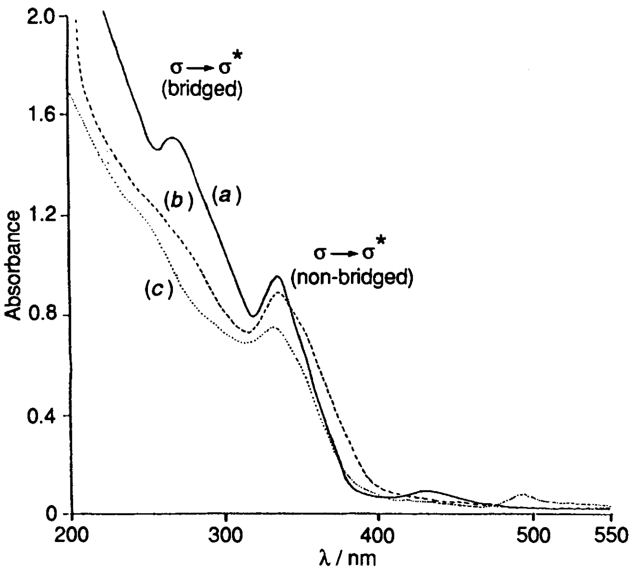
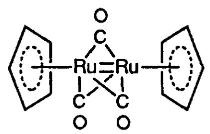


Figure 4. Electronic absorption spectra (Perkin-Elmer Lambda 7) of $[Ru_2(\eta^5-C_5H_5)_2(CO)_4]$: (*a*) in CH_2Cl_2 solution at 298 K, (*b*) after deposition at high dilution in a methane matrix, and (*c*) after irradiation at 12 K using filter C (60 min) + filter D (90 min)



(8)

2 000 and 1 930 cm^{-1} in all matrices is not a CO-loss product. It seems likely that cleavage of the metal–metal bond, predicted for photolysis at these wavelengths, has resulted in small amounts of the radical species $[Ru(\eta^5-C_5H_5)(CO)_2]^{\bullet}$, (7), being isolated in the matrix cage. The analogous iron radical (ν_{CO} 2 004 and 1 938 cm^{-1}) has been observed by Turner and co-workers,[5] and the bands observed here are of similar frequencies and relative intensities to those of the iron radical and to those of matrix-isolated $[Fe(\eta^4-C_4H_6)(CO)_2]$ (ν_{CO} 2 009 and 1 934 cm^{-1} in argon).[23] The assignment is also supported by the fact that on annealing both the bridged and non-bridged isomers are produced on recombination of the radicals.

A second species, (8), was observed in methane and nitrogen matrices which has a single i.r.-active carbonyl stretching band at about 1 830 cm^{-1} and an electronic absorption at $\lambda_{max.}$ = 490 nm. This band is in the bridging region at higher wavenumbers than the bridging CO stretches of (2). These features suggest that this species is the ruthenium analogue of the triply carbonyl-bridged iron dimer, (4). By comparison, (4) has one bridging carbonyl band (ν_{CO} 1 813, methane matrix;[6] 1 812, pvc film;[6] 1 811 cm^{-1}, organic glass[7]) and an electronic absorption band at 505 nm in pvc film. Photolysis into the new electronic band of (8) at 490 nm resulted in a reversal of the photoreaction which is analogous to the behaviour of the iron species. Attempts to confirm the assignment from the i.r. spectra obtained on photolysis of ^{13}CO-enriched (2) were unsuccessful owing to the weakness of the observed bands and their overlapping with the other weak new bands seen at 1 915, 1 853, and 1 806 cm^{-1} produced on photolysis at this wavelength. The nature of the species responsible for these very weak bands and the possible mechanism involved in the observed photochemistry will be discussed below.

(*c*) *Photolysis of* $[Fe_2(\eta^5-C_5H_5)_2(CO)_4]$, (**8**), *in Argon, Methane, and Nitrogen Matrices*.—The i.r. spectrum of compound (1) isolated at high dilution in an argon matrix is shown in Figure 5(*a*). The spectrum is consistent with the presence in the matrix of both the *cis*- and *trans*-bridging isomers (Table 1) by comparison with solution spectra.[24] On photolysis (filter A) into the lowest-energy electronic absorption the bands due to the *trans*-bridged isomer (ν_{CO} 1 962 and 1 792 cm^{-1}) decreased considerably with two strong new bands being produced together at 1 959 and 1 941 cm^{-1} along with a very weak band at 1 819 cm^{-1} [Figure 5(*b*)]. Simultaneously the electronic spectrum showed a clear increase in the shoulder at $\lambda_{max.}$ = 420 nm at the expense of the band at 345 nm [Figure 6(*b*)]. The bands due to the *cis* isomer showed no change throughout the experiment. Photolysis into the new electronic absorption band at 420 nm (filter B) resulted in a weak new band in the i.r. spectrum at 1 998 cm^{-1} at the expense of the parent *trans*-bridged isomer and the new bands at 1 959 and 1 941 cm^{-1} [Figure 5(*c*)]. Higher-energy photolysis (filter D) resulted in the fairly rapid growth of the new i.r. band at 1 819 cm^{-1} and 'free' CO (2 138 cm^{-1}) at the expense of the parent *trans*-bridged isomer [Figure 5(*d*)], with a simultaneously produced new band at 505 nm in the electronic absorption spectrum. Annealing the matrix to about 30 K resulted in all new bands decreasing and the parent i.r. bands increasing in intensity once more. When a similar matrix-isolated sample of compound (1) was photolysed immediately with filter D, with no previous low-energy photolysis, only the new bands at 1 819 and 2 138 cm^{-1} ('free' CO) were seen. Allowing for matrix shifts,

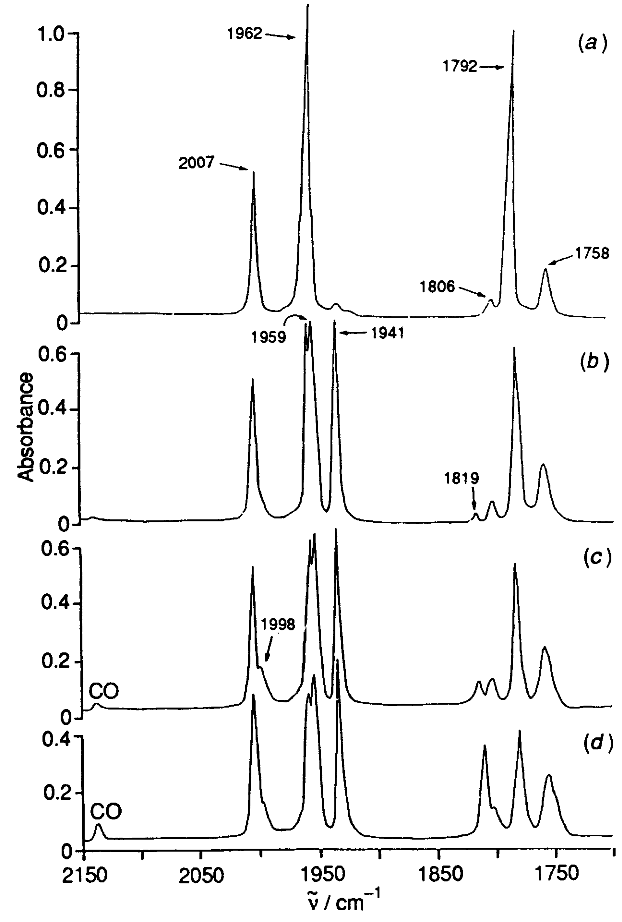


Figure 5. Infrared spectra (Nicolet 7199, resolution 1 cm^{-1}) from an experiment with $[Fe_2(\eta^5-C_5H_5)_2(CO)_4]$ isolated at high dilution in an argon matrix: (*a*) after deposition, (*b*) after irradiation using filter A (20 min), (*c*) after irradiation using filter B(60 min), and (*d*) after irradiation using filter D (30 min)

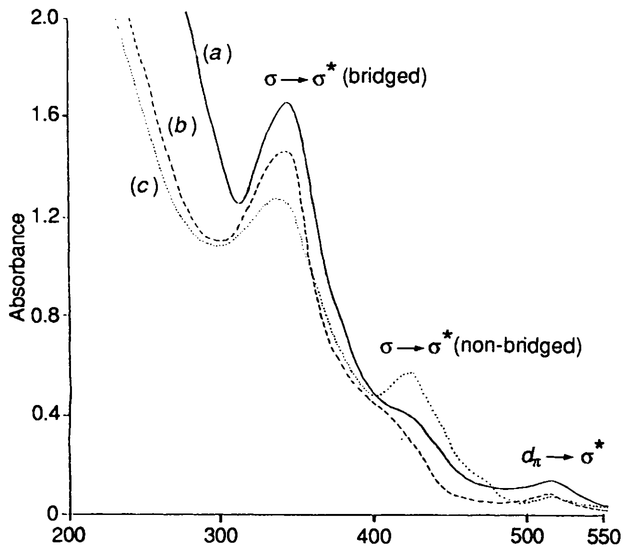


Figure 6. Electronic absorption spectra (Perkin-Elmer Lambda 7) of $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$: (*a*) in CH_2Cl_2 solution at 298 K, (*b*) after deposition at high dilution in a methane matrix, and (*c*) after irradiation at 12 K using filter A (20 min)

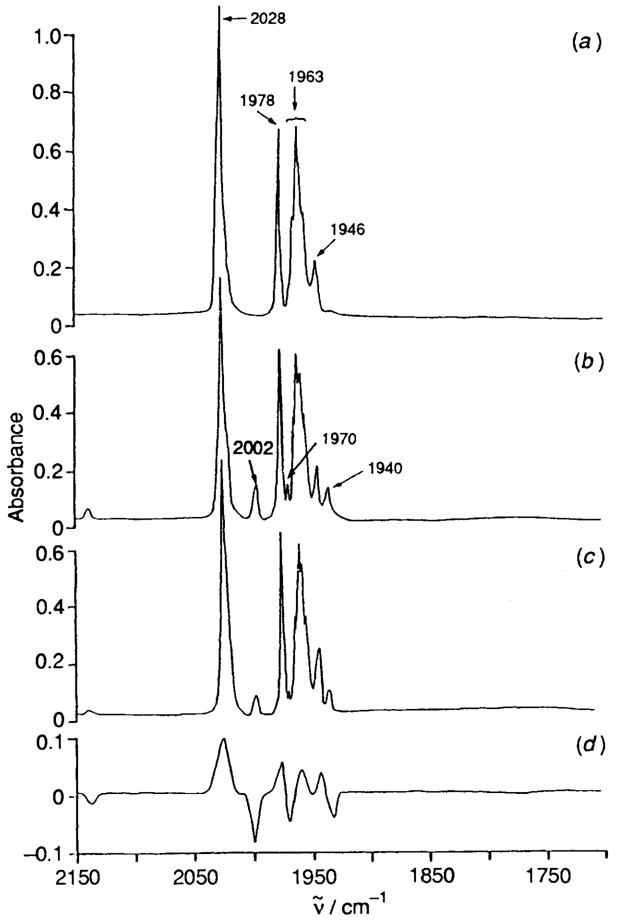


Figure 7. Infrared spectra (Nicolet 7199, resolution 1 cm^{-1}) from an experiment with $[CH_2\{(\eta^5\text{-}C_5H_4)Ru(CO)_2\}_2]$ isolated at high dilution in an argon matrix: (*a*) after deposition, (*b*) after irradiation using filter D (60 min), (*c*) after irradiation using filter B (90 min), and (*d*) subtraction spectrum [(*c*) − (*b*)]

Table 3. Observed positions (cm^{-1}) of CO-stretching modes of compounds (**5**) and (**6**) and their photoproducts in frozen gas matrices at 12 K

Compound	M	Ar	CH_4	N_2
(**5**)	Fe	2 028	2 027	2 027
		1 978	1 975	1 975
		1 963	1 956	1 960
		1 946	1 941	1 944
(**6**)	Ru	2 009	2 005	2 008
		1 975	1 972	1 974
		1 818	1 808	1 815
		1 804	1 794* 1 790	1 798
(**9**)	Ru	2 002	1 997	2 007
		1 970	1 964	1 966
		1 940	1 935	1 936
(**11**)	Fe	1 997	1 991	1 995
		1 934	1 925	1 930
		1 925	1 918	1 926

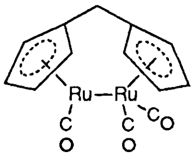
* Matrix splitting.

experiments in both methane and nitrogen matrices produced identical results to those seen in argon (Table 1) and there was no evidence for any dinitrogen co-ordination in the nitrogen matrix.

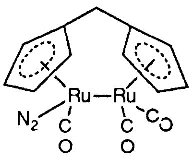
Comparison of the matrix-isolated i.r. and u.v. data (Tables 1 and 2) with previous photochemical studies of compound (**1**) in various media permitted assignment of the species with a bridging CO band at about 1 815 cm^{-1} and a new electronic absorption band at 505 nm as the triply carbonyl-bridged dimer (**4**; R = H). Experiments with filter D described above establish that this species is produced by CO loss from the *trans*-bridged isomer as has been previously suggested.

Low-energy photolysis (filter A: $\lambda > 475$ nm) resulted in the production of another species in all matrices, with two terminal CO stretches of roughly equal intensity at about 1 960 and 1 940 cm^{-1}, and an electronic absorption band at 420 nm. By comparison with the results already seen for compound (**2**) it seems likely that photochemically induced bridge opening of (**1**) is taking place producing a new, all-terminal species. Wrighton and co-workers[10] have predicted that the ($\sigma \longrightarrow \sigma^*$) electronic transition for such a species would be at *ca.* 420 nm which fits the observed data. A non-bridged species would have either C_{2v}, C_{2h}, or C_2 symmetry depending upon whether the CO groups were *cis*, *trans*, or freely rotating giving rise to three, two, and four i.r.-active CO stretching bands, respectively. Since free rotation is unlikely in the gas matrices at about 12 K, and the species is formed from the *trans*-bridged isomer of (**1**), it is not unreasonable to propose that the *trans*-non-bridged isomer of (**1**) has been produced. A non-bridged isomer of (**1**) has been observed in solution with strong terminal CO stretching absorptions at 2 015, 1 973, and 1 938 cm^{-1}.[22] Noack[22b] estimated the concentration of such a species to be about 1% of that of the bridged species at 300 K. These bands are very similar to those observed for the matrix-isolated species. Further, close examination of the sample spectra in freshly prepared matrices indicates a small band at about 1 959 cm^{-1} which could be due to a small amount of the non-bridged isomer being present initially.

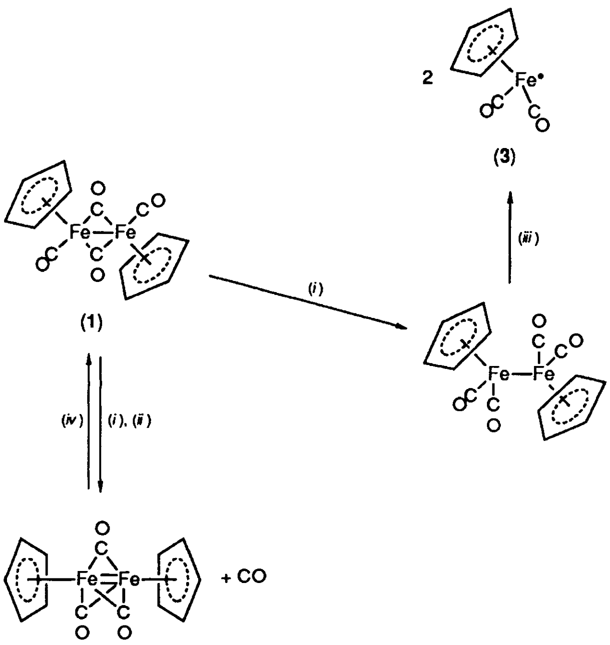
Photolysis into the electronic absorption band (420 nm) of the proposed non-bridged species resulted in the production of a small quantity of a new species which has a carbonyl stretching band at about 2 000 cm^{-1}. This band is in good agreement with the higher-energy carbonyl band of the $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^{\bullet}$ radical species, (**3**), for which Turner and co-workers[12] have reported carbonyl bands at 2 004 and 1 938 cm^{-1}. The second, lower-energy carbonyl band is obscured by



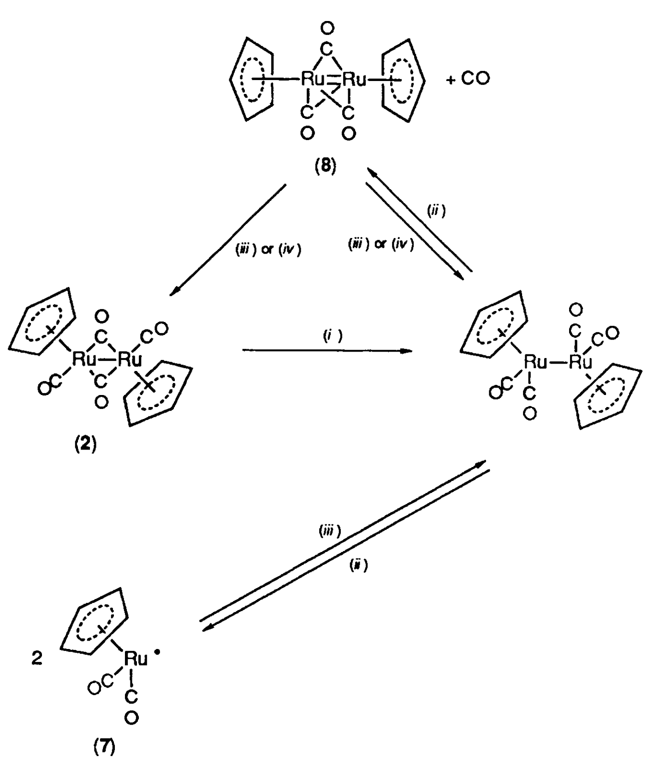
(9)



(10)



Scheme 1. (*i*) *hν*, λ >475 nm; (*ii*) *hν*, 320 < λ < 390 nm; (*iii*) *hν*, λ > 420 nm; (*iv*) heat



Scheme 2. (*i*) *hν*, λ >375 nm; (*ii*) *hν*, 320 < λ < 390 nm; (*iii*) heat; (*iv*) λ > 475 nm

its proximity to a band due to the non-bridged isomer. The radical is probably produced from the non-bridged isomer, but the parent *trans*-bridged isomer continued to undergo bridge opening at the energy used in this photolysis so its concentration is also observed to decrease.

(*d*) *Photolysis of* $[CH_2\{(\eta^5-C_5H_4)Ru(CO)_2\}_2]$, **(6)**, *in Argon, Methane, and Nitrogen Matrices*.—The i.r. spectrum of compound **(6)** isolated at high dilution in an argon matrix is shown in Figure 7(*a*) (Table 3). By comparison with solution i.r. data it is clear that the non-CO bridged isomer of **(6)** has been isolated exclusively in the gas matrix.* Low-energy photolyses (λ > 400 nm) showed no changes in the i.r. spectrum. Higher-energy photolysis (filter D) led to a decrease in all parent bands with the production of three new bands at 2 002, 1 970, and 1 940 cm^{-1} as well as the observation of 'free' CO (2 138 cm^{-1}). Continued photolysis at this and higher energies (filters E and F) only resulted in continued growth of the new bands with a concurrent rise in the 'free' CO band and decreases in the parent band intensities [Figure 7(*b*)]. No new electronic absorption bands could be observed. Subsequent low-energy photolysis (filter B) afforded almost complete photochemical reversal [Figure 7(*c*) and 7(*d*)]. In the methane matrix a similar photolysis pattern was followed and this led to the same species being produced with three terminal CO stretching vibrations at 1 997, 1 964, and 1 935 cm^{-1}.

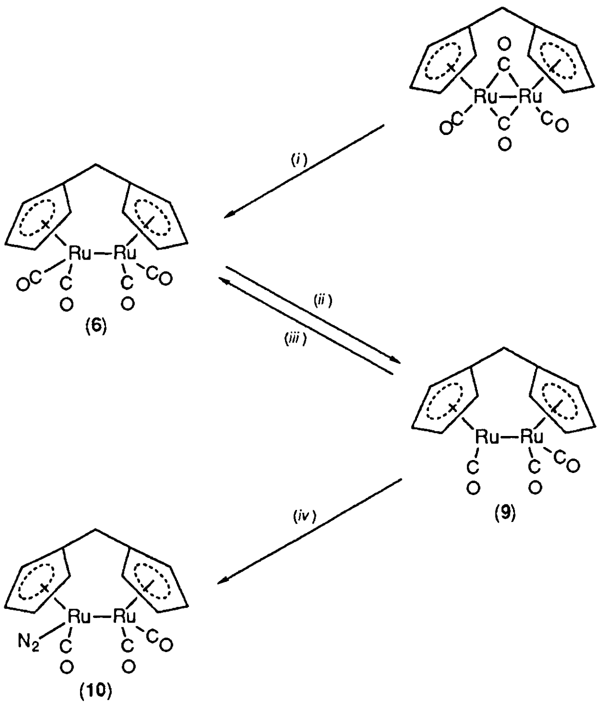
All three bands are apparently due to a single species, produced on CO loss from **(6)**, with three terminal i.r.-active carbonyl stretches. There was no evidence for any bridging carbonyl band at any stage of the experiment, so an analogous species to those produced on CO loss from **(1)** and **(2)** can be ruled out. Homolytic cleavage of the metal–metal bond would not be expected to produce 'free' CO or a species with three carbonyl stretches. The species is also observed to undergo photochemical reversal with CO, and hence it is proposed that the photochemically produced species is the simple, co-ordinatively unsaturated CO-loss species $[Ru_2\{CH_2(\eta^5-C_5H_4)_2\}(CO)_3]$ **(9)**. The low symmetry of this species leads to three i.r.-active terminal carbonyl bands. As expected, the observed CO stretching bands are all at wavenumbers lower than those of the parent dimer, corresponding to an increase in the electron density distributed between the two metal centres.

On photolysis in nitrogen matrices (filter D) a new weak band is observed at 2 175 cm^{-1} in addition to the bands of the CO-loss species at 2 001, 1 967, and 1 936 cm^{-1}. Low-energy photolysis afforded the same reversal of **(9)** to the parent species, however the new band at 2 175 cm^{-1} remained. This band is typical of the stretching frequencies of dinitrogen ligands bound to transition-metal centres. The co-ordinatively unsaturated species **(9)** can apparently react with dinitrogen to produce a co-ordinatively saturated species, $[Ru_2\{CH_2(\eta^5-C_5H_4)_2\}(CO)_3(N_2)]$ **(10)**. The new carbonyl stretches associated with **(10)** would be expected at wavenumbers higher than those of the unsaturated species, but close to those of the parent compound. No additional carbonyl bands associated with the proposed species have been found in the spectra, presumably because of overlapping bands.

(*e*) *Photolysis of* $[CH_2\{(\eta^5-C_5H_4)Fe(CO)_2\}_2]$, **(5)**, *in Argon, Methane, and Nitrogen Matrices*.—In contrast to its ruthenium analogue the spectrum of compound **(5)** in an argon matrix showed that it is present exclusively as the bridged isomer. Low-

---

* There was no evidence in gas matrices for the carbonyl-bridged isomer (ν_{CO} at 1 780 cm^{-1}) observed in low concentrations in solution by Knox *et al.*[25]



Scheme 3. (*i*) Heat in the gas phase; (*ii*) $h\nu$, $320 < \lambda < 390$ nm; (*iii*) $h\nu$, $\lambda > 420$ nm; (*iv*) in nitrogen matrices

energy photolysis (filters A and B) resulted in no change in the i.r. spectrum, nor did photolysis into the $\sigma \longrightarrow \sigma^*$ electronic absorption of the metal–metal bonded bridging system centred at 336 nm (filter E). However, upon high-energy photolysis (filter F) a decrease in the parent bands was observed accompanied by the concomitant appearance of three new terminal carbonyl stretching bands at 1 997, 1 934, and 1 925 cm^{-1} and a band for 'free' CO. A new band was also seen in the electronic spectrum at 425 nm due to the new species and photolysis into this absorption band led to photochemical reversal. In both methane and nitrogen matrices similar high-energy photolyses led to formation of the same species with three CO stretching vibrations at 1 991, 1 925, and 1 918 cm^{-1} in methane and 1 995, 1 930, and 1 926 cm^{-1} in nitrogen.

By analogy with the photochemistry of the ruthenium species (**6**), the photoproduct of (**5**) is believed to be the CO-loss product [$Fe_2\{CH_2(\eta^5\text{-}C_5H_4)_2\}(CO)_3$] (**11**).

Discussion

Photochemical reactions of compounds (**1**) and (**2**) in inert-gas matrices at 12 K have been found to be sensitive to the geometry of the metal complex, its terminal or bridging character, and the wavelength of the exciting radiation (Schemes 1 and 2). Organic glass studies by Wrighton and co-workers[8] and the gas-matrix studies described here demonstrate that, unlike the *trans*-bridged species, the *cis*-bridged isomers of (**1**) and (**2**) do not undergo bridge opening on photolysis at low energies to give all-terminal species. This effect is clearly demonstrated for (**6**) which is forced by the methylene linkage between the cyclopentadienyl rings to remain *cis*, and was found to be exclusively bridged in the matrix. Photolysis of this compound at low energy gives no evidence of the formation of an all-terminal species. Since the steps interconverting *cis*- and *trans*-bridged and -non-bridged iron and ruthenium dimers in solution are well established it would appear that *cis*-bridge opening is a thermally allowed, but photochemically forbidden process, while *trans*-bridge opening is both thermally and photochemically allowed. The theoretical implications of this observation are under investigation.

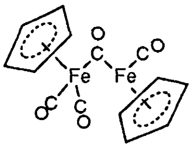
Low-energy bridge opening for *trans*-bridged forms of compounds (**1**) and (**2**) has been observed in argon, methane, and nitrogen matrices. Irradiation of these compounds at low energy converts the *trans*-bridged compounds to all-terminal species characterised by new i.r. bands and, for (**1**), a new electronic absorption consistent with values predicted in the literature. Subsequent photolysis into this new absorption results in homolysis of the iron–iron bond in the all-terminal iron species and the formation of cyclopentadienyliron dicarbonyl radicals. A small amount of the triply carbonyl-bridged species which is observed during this photolysis may arise from a low-efficiency CO loss from the all-terminal dinuclear species, from radical recombination with concurrent CO loss, or from the slight overlap of the high-energy tail of the exciting radiation into the electronic absorption band of the *trans*-bridged species. Since a triply bridging species and radicals are produced by photolysis of (**2**) which is almost exclusively all-terminal, we favour the first two possible explanations for the origins of the triply bridged species. It is also worth noting that the latter is only produced by (**2**) in nitrogen and methane matrices and not in argon. We suggest that the solvent donor capacity of argon is too low to stabilise the as yet uncharacterised intermediate which permits CO loss from either the terminal species or from the radicals to give the triply bridged product. Very weak bands at 1 915, 1 853, and 1 806 cm^{-1} which were observed in methane are tentatively assigned to this intermediate.

Photolysis into the electronic absorption band of the *trans*-bridged isomer of (**1**) results in the direct formation of the triply bridged species which is consistent with the flash photolysis studies of Caspar and Meyer[4] and Turner and co-workers.[5]

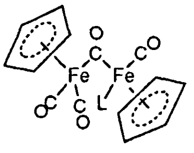
High-energy photolysis of both compounds (**5**) and (**6**) results in the formation of species which exhibit three terminal CO stretches, and 'free' CO, *e.g.* Scheme 3. A new electronic absorption band is observed for the iron compound. Photolysis of the photochemical intermediates at low energy reverses the reaction and reforms starting material. The $^{13}CO/^{12}CO$ exchange on photolysis of 5% ^{13}CO-doped methane matrices supports the assignment of the observed species as photochemical CO-loss products.[21] The new species are apparently asymmetric and may be stabilised by metal–metal double bonds. The geometric constraints imposed by the methylene-linked cyclopentadienyl rings apparently precludes formation of a bridging carbonyl species.

These results which are summarised in Schemes 1 and 2 bear directly on the interpretation of the mechanism of photochemical reactions of compounds (**1**) and (**2**). Preparative photolysis reactions and the photochemical studies of Wrighton and co-workers[10] employ continuous sources which emit light over a broad band of wavelengths. When filters are used they usually establish high-energy cut-offs for irradiation, leaving the low-energy radiation to be passed to the sample. Under these conditions, some triply bridged dinuclear intermediates would be expected to form by direct conversion of the *trans*-bridged species, but, in addition, bridge-opening processes followed by photochemical or thermal homolysis of the metal–metal bond could occur. The latter sequence produces the radicals which have been assumed to characterise the bulk of the photochemistry of these compounds. Flash-photolysis studies presented by Turner and co-workers,[5] and by Bursten *et al.*[14] suggested, in contrast with normal expectations, that the triply bridged species (**4**) was the dominant intermediate in reactions with nucleophiles such as acetonitrile and phosphites rather than the bridged dimer without a Fe–Fe bond, (**12**).

Finally, Gray and co-workers[16] have reported that low-



(12)



(13) L = P(OPr^i)$_3$

energy (λ > 500 nm) photolysis of solutions of compound (**1**) at −78 °C results in the formation of an analogous species characterised as [$(OC)_2(\eta^5-C_5H_5)Fe(\mu-CO)Fe(\eta^5-C_5H_5)(CO)\{P(OPr^i)_3\}$] (**13**) by i.r. and u.v. analysis. Warming this species to room temperature results in the formation of [$Fe_2(\eta^5-C_5H_5)_2(CO)_3L$] products. The photolysis does not appear to involve radicals since the CO-bridged intermediate can be formed in ethyl chloride solution with no formation of [$Fe(\eta^5-C_5H_5)(CO)_2Cl$]. Low-energy photolysis of (**1**) in the presence of chloride donors at room temperature gives the radical product [$Fe(\eta^5-C_5H_5)(CO)_2Cl$].

We have now demonstrated that low-energy photolysis of *trans*-bridged (**1**) results in bridge opening to an all-terminal structure. At room temperature some homolysis of this species by either thermal or photochemical processes can be expected to occur leading to the observed radical products. However, at −78 °C, it is likely that the all-terminal species is stable. We propose that rearrangement of this all-terminal species by the classical process of acyl formation opens up a site on one iron atom for attack of the incoming ligand to give the carbonyl-bridged species observed by Gray. Apparently compound (**2**) with its stronger Ru–Ru bond does not undergo this rearrangement, at least at room temperature, so no similar process is observed.

We believe that it should be possible to adapt the observations made in frozen-gas matrices to preparative applications. For example, low-energy photolyses at −78 °C should afford the all-terminal species, or the μ-CO species available for substitution chemistry. Alternatively, photolyses into the electronic absorption band of *trans*-bridged (**1**) may favour formation of triply bridged dinuclear complexes as intermediates. Specific attempts to employ these findings in synthetic applications are now in progress.

Acknowledgements

We thank the S.E.R.C. for Studentships (to P. E. B., A. K. C., and R. H. H.) and for support (to A. J. R.). We also thank the Naval Academy Research Council for support (to T. E. B. and J. E. S.) and the Naval Academy Faculty Development Fund for Sabbatical Travel support (to T. E. B.).

References

1 E. D. Jemmis, A. R. Pinhas, and R. Hoffman, *J. Am. Chem. Soc.*, 1980, **102**, 2576; M. Benard, *Inorg. Chem.*, 1979, **18**, 2782.
2 (*a*) G. L. Geoffroy and M. S. Wrighton, 'Organometallic Photochemistry,' Academic Press, New York, 1979; (*b*) J. V. Caspar and T. J. Meyer, *Chem. Rev.*, 1985, **85**, 187; (*c*) M. J. Winter, *Adv. Organomet. Chem.*, 1989, **29**, 101.
3 R. H. Hooker, K. A. Mahmoud, and A. J. Rest, *J. Organomet. Chem.*, 1983, **254**, C25.
4 J. V. Caspar and T. J. Meyer, *J. Am. Chem. Soc.*, 1980, **102**, 7795.
5 B. D. Moore, M. B. Simpson, M. Poliakoff, and J. J. Turner, *J. Chem. Soc., Chem. Commun.*, 1984, 972.
6 (*a*) R. H. Hooker, K. A. Mahmoud, and A. J. Rest, *J. Chem. Soc., Chem. Commun.*, 1983, 1022; (*b*) R. H. Hooker and A. J. Rest, *J. Chem. Soc., Dalton Trans.*, 1990, 1221.
7 A. F. Hepp, J. P. Blaha, C. Lewis, and M. S. Wrighton, *Organometallics*, 1984, **3**, 174.
8 J. P. Blaha, B. E. Bursten, J. C. Dewan, R. B. Frankel, C. L. Rudolph, B. A. Wilson, and M. S. Wrighton, *J. Am. Chem. Soc.*, 1985, **107**, 4561.
9 R. J. Haines and A. L. DuPreez, *Inorg. Chem.*, 1969, **8**, 1459.
10 H. A. Abrahamson, M. C. Palazzotto, C. L. Reichel, and M. S. Wrighton, *J. Am. Chem. Soc.*, 1979, **101**, 4123.
11 A. J. Dixon, M. A. Healy, M. Poliakoff, and J. J. Turner, *J. Chem. Soc., Chem. Commun.*, 1986, 944.
12 A. J. Dixon, S. J. Gravelle, L. J. Van de Burgt, M. Poliakoff, J. J. Turner, and E. Weitz, *J. Chem. Soc., Chem. Commun.*, 1987, 1023.
13 J. N. Moore, P. A. Hansen, and R. M. Hochstrasser, *J. Am. Chem. Soc.*, 1989, **111**, 4563.
14 B. E. Bursten, S. D. McKee, and M. S. Platz, *J. Am. Chem. Soc.*, 1989, **111**, 3428.
15 B. E. Bursten and R. H. Cayton, *J. Am. Chem. Soc.*, 1986, **108**, 8241.
16 D. R. Tyler, M. A. Schmidt, and H. B. Gray, *J. Am. Chem. Soc.*, 1983, **105**, 6018; 1979, **101**, 2753.
17 (*a*) A. S. Goldman and D. R. Tyler, *Inorg. Chem.*, 1987, **26**, 253; (*b*) M. P. Castellani and D. R. Tyler, *Organometallics*, 1989, **8**, 2113.
18 D. H. Gibson, W-L. Hsu, A. L. Steinmetz, and B. V. Johnson, *J. Organomet. Chem.*, 1981, **208**, 89.
19 T. E. Bitterwolf, *J. Organomet. Chem.*, 1986, **312**, 197.
20 W. A. G. Graham, J. K. Hoyano, A. D. McMaster, A. J. Rest, and I. Whitwell, *J. Chem. Soc., Dalton Trans.*, 1987, 1181.
21 R. H. Hooker and A. J. Rest, *J. Chem. Soc., Dalton Trans.*, 1984, 761.
22 (*a*) R. D. Fischer, A. Vogler, and K. Noack, *J. Organomet. Chem.*, 1967, **7**, 135; (*b*) K. Noack, *ibid.*, p. 151; (*c*) P. McArdle and A. R. Manning, *J. Chem. Soc. A*, 1970, 2128.
23 G. Ellerhorst, W. Gerhartz, and F. W. Grevels, *Inorg. Chem.*, 1980, **19**, 67.
24 J. G. Bullitt, F. A. Cotton, and T. J. Marks, *Inorg. Chem.*, 1972, **11**, 671; *J. Am. Chem. Soc.*, 1970, **92**, 2155.
25 S. A. R. Knox, K. A. Macpherson, A. G. Orpen, and M. C. Rendle, *J. Chem. Soc., Dalton Trans.*, 1989, 1807.

Received 9*th April* 1990; *Paper* 0/01587C