Comparative Photochemistry of Some Tricarbonyl(η^4-polyene)iron Complexes in Frozen Gas Matrices at *ca.* 12 K†

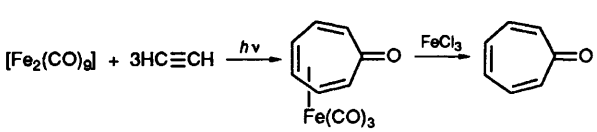
Stephen T. Astley, Mary P. V. Churton, Ramli B. Hitam, and Antony J. Rest*
Department of Chemistry, The University, Southampton SO9 5NH

Ultraviolet irradiation of [Fe(η^4-polyene)(CO)$_3$] complexes [polyene = 1,3-butadiene (C_4H_6), cyclobutadiene (C_4H_4), 2,4-cyclopentadien-1-one (C_4H_4CO), cyclopentadiene (C_5H_6), 1,3-cyclohexadiene (C_6H_8), 1,3-cycloheptadiene (C_7H_{10}), 1,3-cyclo-octadiene (C_8H_{12}), or 1,3,5,7-cyclo-octatetraene (C_8H_8)] in frozen gas matrices at *ca.* 12 K results in two competing processes. One is partial dechelation of the polyene ligand to form [Fe(η^2-polyene)(CO)$_3$] species and the other is dissociation of a CO ligand to produce co-ordinatively unsaturated [Fe(η^4-polyene)(CO)$_2$] species. The photogenerated species were characterised by i.r. spectroscopy. Evidence is presented which indicates that [Fe(η^2-polyene)(CO)$_3$] species are responsible for *s-cis* $\rightleftharpoons$ *s-trans*, 'tub' $\rightleftharpoons$ 'chair', and $\pi \rightleftharpoons \sigma$ rearrangements in [Fe(η^4-C_4H_6)(CO)$_3$], [Fe(η^4-C_8H_8)(CO)$_3$], and [Fe(η^4-C_4H_4)(CO)$_3$] respectively. The possibility of ring opening to form a metallocyclic intermediate is discussed in relation to the photoconversion of [Fe(η^4-C_4H_4)(CO)$_3$] into [Fe(η^4-C_4H_4CO)(CO)$_3$] in a carbon monoxide matrix. In a ^{13}CO-doped methane matrix, facile ^{13}CO/^{12}CO exchange occurred for the Fe(CO)$_3$ fragment of [Fe(η^4-C_4H_4CO)(CO)$_3$] but no exchange was found for the ketonic CO group. Ring-to-metal hydrogen migration forming [Fe(η^5-C_5H_5)(CO)$_2$H] and [Fe(η^5-C_7H_9)(CO)$_2$H] has been found to occur for [Fe(η^4-C_5H_6)(CO)$_3$] and [Fe(η^4-C_7H_{10})(CO)$_3$] complexes *via* the co-ordinatively unsaturated fragments [Fe(η^4-C_5H_6)(CO)$_2$] and [Fe(η^4-C_7H_{10})(CO)$_2$]. The intermediacy of η^2-bound polyene species of the type [Fe(η^2-polyene)(CO)$_4$] has been established in the photodissociation of polyene ligands and the formation of [Fe(CO)$_5$] in carbon monoxide matrices.

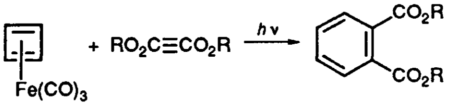
Many zero-oxidation-state iron complexes are known in which unsaturated hydrocarbons are bonded to Fe(CO)$_3$ fragments. In such complexes a 1,3-diene unit is π-bonded to the metal, *e.g.* (η^4-1,3-butadiene)tricarbonyliron, but there may be uncomplexed double bonds, *e.g.* [tricarbonyl(η^4-cyclo-octatetraene)iron].[1] The [Fe(η^4-diene)(CO)$_3$] complexes, or more generally [Fe(η^4-polyene)(CO)$_3$], undergo a wide variety of thermal and photochemical reactions [*e.g.* equations (1)—(3)] some of which are important in the context of large- and small-scale syntheses of organic compounds *via* iron carbonyl reagents.[2]

The matrix-isolation technique[3] is a powerful weapon for probing the mechanisms of reactions because unstable species,[4] particularly those proposed as intermediates in organometallic reactions,[5] can be trapped and characterised at low temperatures. In this paper the comparative photochemistry of [Fe(η^4-polyene)(CO)$_3$] complexes [polyene = 1,3-butadiene (C_4H_6), cyclobutadiene (C_4H_4), 2,4-cyclopentadien-1-one (C_4H_4CO), cyclopentadiene (C_5H_6), 1,3-cyclohexadiene (C_6H_8), 1,3-cycloheptadiene (C_7H_{10}), 1,3-cyclo-octadiene (C_8H_{12}), or 1,3,5,7-cyclo-octatetraene (C_8H_8)] is described in various gas matrices at *ca.* 12 K.

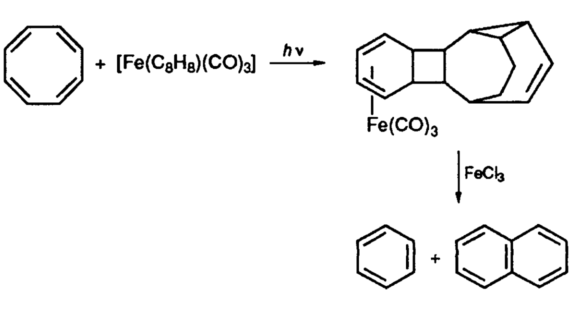
Previous studies of the photoreactions of [Fe(η^4-polyene)(CO)$_3$] complexes and especially [Fe(η^4-C_4H_4)(CO)$_3$] (**2**) in gas matrices at *ca.* 12 K all used very broad band-pass irradiation sources. Some new insights have been revealed, therefore, as a result of carrying out narrower band-pass irradiations using a variety of filters. The results are related to previous studies which have now been found to be incomplete, *e.g.* [Fe(η^4-C_4H_6)(CO)$_3$],[6] [Fe(η^4-C_4H_4)(CO)$_3$],[7,8] and [Fe(η^4-C_8H_8)(CO)$_3$],[9] to other matrix studies of [Fe(η^4-diene)(CO)$_3$] complexes (diene = cyclopentadiene or 5,5-dimethylcyclopentadiene),[10] and to the thermal and photochemical reactions of [Fe(η^4-polyene)(CO)$_3$] complexes in solution.[11–21] The preliminary report[22] of the photochemical insertion of a bound CO ligand into the cyclobutadiene ring of [Fe(η^4-C_4H_4)(CO)$_3$] has been confirmed and extended.



(1)



(2)



(3)

Experimental

The cryogenic equipment and vacuum system, matrix-deposi-

---

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

Table 1. Electronic absorption band positions ($\lambda_{max.}$/nm)* for [Fe(η^4-polyene)(CO)$_3$] complexes (polyene = C_4H_6, C_4H_4, C_4H_4CO, C_7H_{10}, or C_8H_8) in argon matrices at *ca.* 12 K

Compound	Charge-transfer transition	*d–d* Transition
(**1**) [Fe(η^4-C_4H_6)(CO)$_3$]	210s	295m
(**2**) [Fe(η^4-C_4H_4)(CO)$_3$]	225s	290m
(**3**) [Fe(η^4-C_4H_4CO)(CO)$_3$]	220s	300m, 340m
(**6**) [Fe(η^4-C_7H_{10})(CO)$_3$]	210s	285m, *ca.* 400w
(**8**) [Fe(η^4-C_8H_8)(CO)$_3$]	260s	300m, *ca.* 410w

* w = weak, m = medium, and s = strong.

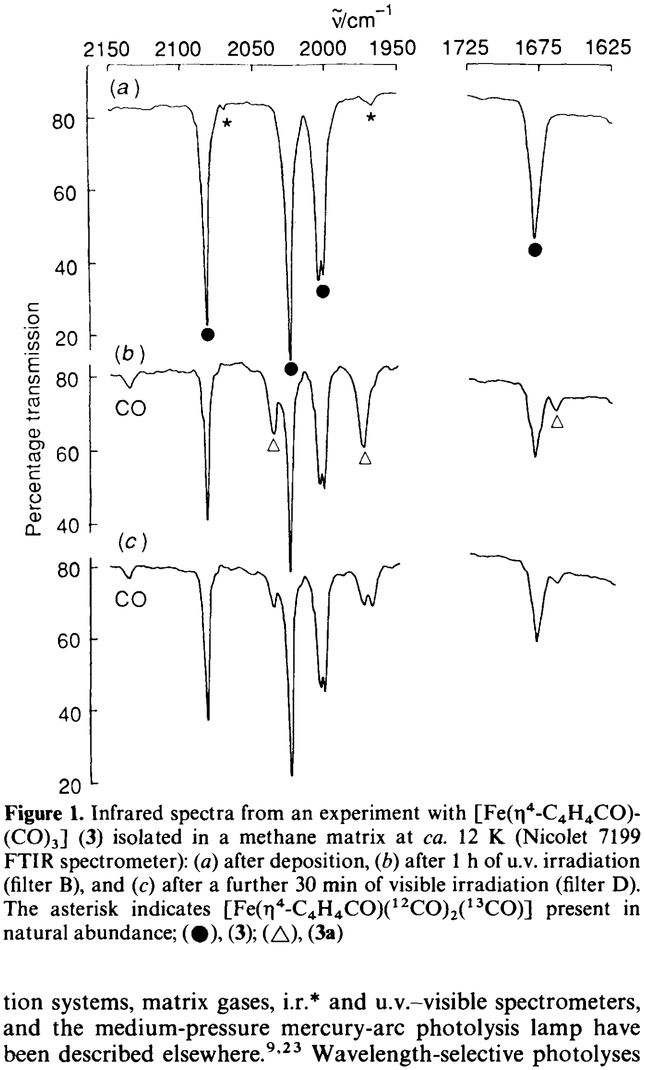


Figure 1. Infrared spectra from an experiment with [Fe(η^4-C_4H_4CO)(CO)$_3$] (**3**) isolated in a methane matrix at *ca.* 12 K (Nicolet 7199 FTIR spectrometer): (*a*) after deposition, (*b*) after 1 h of u.v. irradiation (filter B), and (*c*) after a further 30 min of visible irradiation (filter D). The asterisk indicates [Fe(η^4-C_4H_4CO)(^{12}CO)$_2$(^{13}CO)] present in natural abundance; (●), (**3**); (△), (**3a**)

tion systems, matrix gases, i.r.* and u.v.–visible spectrometers, and the medium-pressure mercury-arc photolysis lamp have been described elsewhere.[9,23] Wavelength-selective photolyses in this study were achieved by using the following combinations of absorbing materials: filter A, $230 < \lambda < 280$ nm, quartz gas cell (pathlength 25 mm) containing Cl_2 (2 atm) + Corning colour filter CS 7-54 (3 mm thick); filter B, $230 < \lambda < 390$ nm, Corning colour filter CS 7-54 (3 mm thick); filter C, $320 < \lambda < 390$ nm, Corning colour filter CS 7-60 (3 mm thick); filter D, $\lambda > 420$ nm, Corning colour filter CS 3-74 (3 mm thick); filter E, $290 < \lambda < 370$ and $\lambda > 550$ nm, quartz gas cell (pathlength 25 mm) containing Br_2 (300 Torr) + Pyrex disc (3 mm thick); filter F, $\lambda < 370$ nm and $\lambda > 550$ nm, quartz gas cell (pathlength 25 mm) containing Br_2 (300 Torr); filter G, $\lambda > 330$ nm, soda glass disc (4 mm thick); filter H, $\lambda < 280$ nm and $\lambda > 550$ nm, quartz gas cell (pathlength 25 mm) containing Cl_2 (2 atm) + quartz gas cell (pathlength 25 mm) containing Br_2 (300 Torr).

The samples of [Fe(η^4-C_4H_4)(CO)$_3$], [Fe(η^4-C_4H_4CO)(CO)$_3$], and [Fe(η^4-C_8H_8)(CO)$_3$] were gifts (see Acknowledgements) and were used without purification. They were found to have no impurities. Samples of [Fe(η^4-C_5H_6)(CO)$_3$],[24] [Fe(η^4-C_6H_8)(CO)$_3$],[25] [Fe(η^4-C_7H_{10})(CO)$_3$],[26] and [Fe(η^4-C_8H_{12})(CO)$_3$][27] were prepared according to literature procedures. Product mixtures were separated by column chromatography and vacuum distillation.

Matrices containing [Fe(η^4-C_5H_6)(CO)$_3$], [Fe(η^4-C_6H_8)(CO)$_3$], and [Fe(η^4-C_7H_{10})(CO)$_3$] were prepared by making gas mixtures of the complex and matrix gas of the required composition (1:2 000 to 1:5 000) using a vacuum line and standard manometric techniques and depositing the gas mixture onto the cooled CsI window by the 'pulsed' technique.[28] The complexes [Fe(η^4-C_8H_{12})(CO)$_3$] and [Fe(η^4-C_4H_4CO)(CO)$_3$] were less volatile but subliming them from glass fingers held at 20 and 45—50 °C respectively provided vapour which was co-condensed with a large excess of matrix gas from a bulb *via* a needle valve onto the cold CaF_2 and CsI windows.

Results

The photoreactions of the [Fe(η^4-polyene)(CO)$_3$] complexes in matrices at *ca.* 12 K fell into two categories: (*a*) those with an *even* number of carbon atoms and (*b*) those with an *odd* number of carbon atoms. Within these categories, and in order to present the work concisely, general photoreactions will be described using a typical complex. The photoreactions specific to particular complexes will be described separately.

Photolysis of the complexes employed filters to match the irradiation wavelengths with the electronic absorption band maxima of the complexes (Table 1).

(*a*) *Photolysis of* [Fe(η^4-C_4H_6)(CO)$_3$] (**1**), [Fe(η^4-C_4H_4)(CO)$_3$] (**2**), [Fe(η^4-C_4H_4CO)(CO)$_3$] (**3**), [Fe(η^4-C_6H_8)(CO)$_3$] (**5**), [Fe(η^4-C_8H_{12})(CO)$_3$] (**7**), *and* [Fe(η^4-C_8H_8)(CO)$_3$] (**8**) *in Frozen Gas Matrices at* ca. 12K.—(*i*) *Argon and methane matrices.* The i.r. spectrum of [Fe(η^4-C_4H_4CO)(CO)$_3$] (**3**) isolated at high dilution in a methane matrix showed three strong absorption bands in the terminal CO-stretching region at 2 083 (*A*′), 2 025 (*A*′), and 2 003 (*A*″) cm^{-1} for a C_s† symmetry Fe(CO)$_3$ fragment[31] and a band at 1 679 cm^{-1} due to the ketonic CO-stretching band of the cyclopentadienone ring [Figure 1(*a*), Table 2]. On u.v. irradiation (filter B) four new bands grew in intensity at 2 138 ('free' CO), 2 037, 1 974, and

---

* The effective resolutions for the Nicolet 7199 FTIR and Grubb Parsons Spectromajor grating spectrometers were both 1 cm^{-1}. Subtraction of spectra using the Nicolet computer was carried out in absorbance mode and then the results converted back to percentage transmissions.

† A normal-co-ordinate analysis[29] and the solution spectra[30] have shown that the Fe(CO)$_3$ moieties in [Fe(η^4-polyene)(CO)$_3$] complexes have C_{3v} local symmetry, giving rise to two terminal CO stretching bands. This symmetry assignment has been supported by energy-factored force-field fitting calculations. In gas matrices, however, the splitting of the *E* mode [Figures 1(*a*) and 2(*a*)] arising from the much higher resolution achievable in gas matrices (half-width at half-height < 1 cm^{-1}) either reveals subtle conformational effects not observed in solution spectra at 298 K or it might indicate a slight distortion due to the packing of host matrix molecules around the substrate. The latter effect results[3] in band splittings up to *ca.* 10 cm^{-1}. The *ca.* 20 cm^{-1} splittings for the [Fe(η^4-polyene)(CO)$_3$] complexes in this work indicate the freezing out of polyene rotations which are rapid at ambient temperatures.

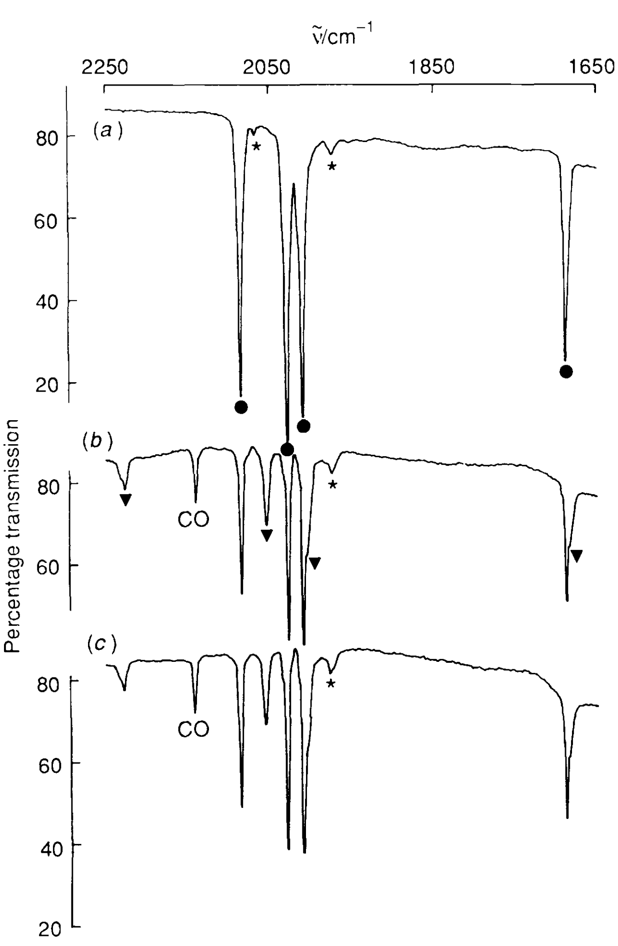


Figure 2. Infrared spectra from an experiment with [Fe(η^4-C_4H_4CO)($CO)_3$] (3) isolated in a nitrogen matrix at *ca.* 12 K (Nicolet 7199 FTIR spectrometer): (*a*) after deposition, (*b*) after 5 h of u.v. irradiation (filter B), and (*c*) after 30 min of visible irradiation (filter D). The asterisk indicates [Fe(η^4-C_4H_4CO)($^{12}CO)_2$(^{13}CO)] present in natural abundance; (●), (**3**); (▼), (**3b**)

1 664 cm^{-1} while the bands of (3) diminished in intensity [Figure 1(*b*)]. On visible light irradiation (filter D) reversal occurred [Figure 1(*c*)]. Since the new bands grew and reversed with constant relative intensities they can be assigned to a single new photoproduct. The retention of a new band which can be assigned to a ketonic CO-stretching band (1 664 cm^{-1}) while at the same time observing 'free' CO both point toward a co-ordinatively unsaturated 16-electron species, *i.e.* the new photoproduct is [Fe(η^4-C_4H_4CO)($CO)_2$] (**3a**). Analogous observations were recorded for argon matrices (Table 2) and at no time was migration of a CO from the cyclopentadienone ring to the metal found to occur.

Reversible ejection of CO, which was more facile in methane than argon matrices, was also observed for complexes (**1**), (**2**), (**5**), (**7**), and (**8**) although the yield for (**7**) was very small (Table 2).

(*ii*) *Nitrogen matrices.* U.v. irradiation (filter B) of complex (**3**) [ν_{CO} at 2 084 (*A*'), 2 027 (*A*'), and 2 007 (*A*") and ν_{CO}(ketonic) at 1 686 cm^{-1} in nitrogen matrices] caused a reduction in the intensities of the parent bands and the growth of new bands at 2 226, 2 138 ('free' CO), and 2 053 cm^{-1} together with shoulder bands at 2 002 and 1 682 cm^{-1} [Figure 2(*b*)]. The observation of 'free' CO and a band at *ca.* 2 225 cm^{-1} indicates that photosubstitution of CO by N_2 has taken place, *i.e.* the new species is [Fe(η^4-C_4H_4CO)($CO)_2$(N_2)] (**3b**). On irradiation with visible light (filter D) reversal occurred. This behaviour together with the high wavenumbers of the NN-stretching band suggest that the new dinitrogen species might not be thermally stable at ambient temperatures.

Similar observations were recorded for complexes (**1**), (**2**), (**5**), (**7**), and (**8**). In some cases [(**2**), (**5**)] prolonged photolysis afforded substitution of a second N_2 ligand (Table 2).

(*iii*) *Carbon monoxide matrices.* U.v. irradiation (filter A) of [Fe(η^4-C_4H_6)($CO)_3$] (**1**) isolated in a CO matrix [Figure 3(*a*)] caused the parent bands to decrease in intensity while four new bands at 2 026, 2 003, 1 965, and 1 944 cm^{-1} gradually appeared [Figure 3(*b*)]. On further photolysis with visible light (filter D), however, the bands all decreased in intensity and two additional bands at 2 014 and 2 009 cm^{-1} emerged [Figure 3(*c*)]. The latter pair of new bands disappeared upon further u.v. photolysis (filter H) [Figure 3(*d*)]. From the behaviour of the new product bands, *i.e.* increasing and decreasing together, there seem to be at least three photoproducts. The bands at 2 026, 1 965, and 1 944 cm^{-1} may be assigned to [Fe(η^2-C_4H_6)($CO)_3$] (**1c**) by comparison with bands for argon and methane matrices (Table 2). Similarly the bands at 2 014 and 2 009 cm^{-1} may be compared with the bands previously assigned to [Fe(η^2-C_4H_6)($CO)_4$] (**1d**) (ν_{CO} at 2 088m, 2 018vs, and 1 988vs cm^{-1} in Ar at 10 K).[6] The identification of (**1d**) on the basis of bands at 2 014, and 2 009 cm^{-1} is consistent with the previous study because the 2 088 cm^{-1} region is obscured by naturally occurring ^{13}CO while the 1 988 cm^{-1} region contains a strong band of (**1**). Further comparison with photolysis studies in CH_4 (see above) showed that the band at 2 026 cm^{-1} was approximately three times more intense in CO than in CH_4. This anomaly indicates overlapping bands. A plausible assignment is that the overlapped band at 2 026 cm^{-1} belongs with the band at 2 003 cm^{-1} and that these bands are due to [Fe($CO)_5$]. Support from this proposition comes from experiments with [Fe($CO)_5$] in various matrices (ν_{CO} at 2 028, 2 004, and 1 996 cm^{-1} in various gas matrices);[32] the lowest band of [Fe($CO)_5$] would be hidden under the band of (**1**) at 1 989 cm^{-1} or appear as a shoulder on this band.

Similar results were obtained for complexes (**7**) and (**8**) (Table 2). Attempts to photolyse (**5**) in carbon monoxide matrices were unsuccessful indicating that the C_6H_8 ring is reluctant to undergo ring slippage. Irradiation of (**2**) in such matrices gave (**3**)[22] which did not undergo further CO insertion into the C_4H_4CO ring to give a η^4-quinone complex.

(*iv*) *Photolysis of* [Fe(η^4-C_4H_4)($CO)_3$] (**2**) *in argon and methane matrices at* ca. 12 K. A period of u.v. irradiation (filter A) of complex (**2**) isolated at high dilution in a methane CH_4 matrix at *ca.* 12 K [Figure 4(*a*)] led to the growth of bands [Figure 4(*b*)] attributable [see section (*a*) (*i*)] to the 16-electron species [Fe(η^4-C_4H_4)($CO)_2$] (**2a**) (ν_{CO} at 1 993 and 1 926 cm^{-1}, Table 2).[8] Further photolysis with longer-wavelength radiation (filter C) caused reversal to regenerate (**2**) [Figure 4(*c*)]. When the matrix was irradiated with both u.v. and near-visible radiation (filter B) for a long period of time, however, four additional new bands at 2 035, 2 027, 1 975, and 1 968 cm^{-1} gradually appeared until after 7 h they were almost as intense as the bands of the parent complex (**2**) [Figure 4(*d*)]. Photolysis then with visible light (filter D) reversed the bands of (**2a**) together with 'free' CO with simultaneous increases in the bands of (**2**) and in the bands at 2 027 and 1 968 cm^{-1} [Figure 4(*e*)]. Photolysis now with the original u.v. irradiation (filter A) resulted in the growth of bands at 2 035 and 1975 cm^{-1} together with those due to (**2a**) and 'free' CO while the bands for (**2**) and those at 2 027 and 1 968 cm^{-1} decreased [Figure 4(*f*)]. From the behaviour of the bands under a variety of photolyses it is clear that there are two photoproducts formed in addition to the originally observed[7,8] co-ordinatively unsaturated 16-electron species, (**2a**). The two new species (**2c**) and (**2d**) may be associated with pairs of bands at 2 035/1 975 and 2 027/1 968 cm^{-1} respectively. Annealing the matrix to *ca.* 35 K produced

Table 2. Observed i.r.-active terminal stretching bands (cm^{-1}) for $[Fe(\eta^4\text{-polyene})(CO)_3]$ complexes (polyene = C_4H_6, C_4H_4, C_4H_4CO, C_5H_6, C_6H_8, C_7H_{10}, C_8H_{12}, or C_8H_8) and their photoproducts in various gas matrices at *ca.* 12 K

	Compound	CH_4	Ar^a	N_2^{a}	CO	
(1)	$[Fe(\eta^4\text{-}C_4H_6)(CO)_3]$	2 054 1 985 1 976^b	2 060 1 995 1 983	2 058 1 995 1 981	2 057 1 989 1 979	
(1a)	$[Fe(\eta^4\text{-}C_4H_6)(CO)_2]$	2 000 1 935	2 009 1 944			
(1b)^c	$[Fe(\eta^4\text{-}C_4H_6)(CO)_2(N_2)]$			2 018 1 971		
(1c)	$[Fe(\eta^2\text{-}C_4H_6)(CO)_3]$	2 024 1 964 1 942	2 029 1 970 1 953	2 027 1 967 1 946	2 026^d 1 965 1 944	
(1d)	$[Fe(\eta^2\text{-}C_4H_6)(CO)_4]$				2 014 2 009	
(2)	$[Fe(\eta^4\text{-}C_4H_4)(CO)_3]$	2 057 1 988 1 979^b	2 050 1 981 1 972^b	2 055 1 987 1 981 1 977 } *b*	2 054 1 985 1 976^b	
(2a)	$[Fe(\eta^4\text{-}C_4H_4)(CO)_2]$	1 993 1 926	2 003 1 936			
(2b)^e	$[Fe(\eta^4\text{-}C_4H_4)(CO)_2(N_2)]$			2 013 2 012 } *f* 1 963 1 959 } *f*		
(2c)	$[Fe(\eta^2\text{-}C_4H_4)(CO)_3]$	2 035 1 975	2 039 1 976			
(2d)	$[Fe(\sigma,\sigma'\text{-}C_4H_4)(CO)_3]$	2 027 1 968	2 031 1 972			
(2e)	$[Fe(\eta^3,\sigma\text{-}C_4H_4)(CO)_3]$	2 020 1 960	2 028 1 969			
(3)	$[Fe(\eta^4\text{-}C_4H_4CO)(CO)_3]$	2 083 2 025 2 003 1 679^h	2 086 2 017 2 005 1 690^h	2 084 2 027 2 007 1 686^h	2 082 2 026 2 006 1 677^h	(2 082)^g (2 025) (2 006) (1 677)^h
(3a)	$[Fe(\eta^4\text{-}C_4H_4CO)(CO)_2]$	2 037 1 974 1 664^h	2 038 1 975 1 675^h			
(3b)^i	$[Fe(\eta^4\text{-}C_4H_4CO)(CO)_2(N_2)]$			2 053 2 002 1 682^h		
(4)	$[Fe(\eta^4\text{-}C_5H_6)(CO)_3]$	2 048 1 980 1 970			2 050 1 982 1 974	
(4a)	$[Fe(\eta^4\text{-}C_5H_6)(CO)_2]$	1 991 1 926				
(4c)	$[Fe(\eta^2\text{-}C_5H_6)(CO)_3]$				2 038 1 962 1 953	
(4d)^j	$[Fe(\eta^2\text{-}C_5H_6)(CO)_4]$				2 004^j 1 997	
(4e)	$[Fe(\eta^5\text{-}C_5H_5)(CO)_2H]$	2 020 1 963			2 025 1 967	
(4f)^j	$[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^{\bullet}$				1 940	
(5)	$[Fe(\eta^4\text{-}C_6H_8)(CO)_3]$	2 054 1 983 1 976		2 058 1 988 1 985	2 056 1 984 1 980	
(5a)	$[Fe(\eta^4\text{-}C_6H_8)(CO)_2]$	1 999 1 933				
(5b)^{k,l}	$[Fe(\eta^4\text{-}C_6H_8)(CO)_2(N_2)]$		2 013 1 968			
(6)	$[Fe(\eta^4\text{-}C_7H_{10})(CO)_3]$	2 047 1 979 1 976 1 973 } *b*	2 054 1 986 1 983 1 978 } *b*	2 052 1 984 1 982 } *b*	2 050 1 982 1 978 } *b*	
(6′)		2 045 1 977 1 976 1 970 } *b*	2 051 1 983 1 981 1 979 1 977 } *b*	2 050 1 983 1 978 } *b*	2 047 1 979 1 976 } *b*	
(6a)	$[Fe(\eta^4\text{-}C_7H_{10})(CO)_2]$	1 994 1 930	1 989 1 933			
(6a′)		1 992 1 927	1 998 1 932			

Table 2 (*continued*)

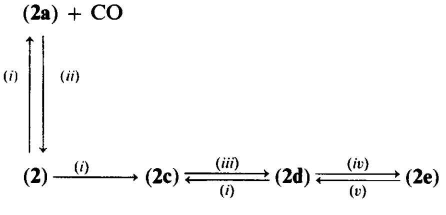
	Compound	CH_4	Ar[a]	N_2[a]	CO
(6b)[m]	$[Fe(\eta^4\text{-}C_7H_{10})(CO)_2(N_2)]$			2 009	
				1 961	
(6e)	$[Fe(\eta^5\text{-}C_7H_9)(CO)_2H]$	2 016	2 020		
		1 961	1 967		
(7)	$[Fe(\eta^4\text{-}C_8H_{12})(CO)_3]$		2 054	2 055	2 053
			1 988	1 986	1 984
			1 981	1 983	1 980
(7a)	$[Fe(\eta^4\text{-}C_8H_{12})(CO)_2]$		2 000		
			1 935		
(7b)[n]	$[Fe(\eta^4\text{-}C_8H_{12})(CO)_2(N_2)]$			2 015	
				1 965	
(7c)[j]	$[Fe(\eta^2\text{-}C_8H_{12})(CO)_4]$				2 088
					2 040
(8)	$[Fe(tub\text{-}\eta^4\text{-}C_8H_8)(CO)_3]$	2 053	2 059	2 056	2 055
		1 991[b]	1 997	1 999	1 997
		1 975[b]	1 982	1 983	1 981
(8′)	$[Fe(chair\text{-}\eta^4\text{-}C_8H_8)(CO)_3]$	2 059	2 065	2 063	2 061
		1 998[b]	2 006	2 002	2 000
		1 987	1 993	1 994	1 990
(8a)	$[Fe(\eta^4\text{-}C_8H_8)(CO)_2]$	1 993	2 001	1 999	1 996[c]
		1 928	1 935	1 932	1 928
(8b)[o]	$[Fe(\eta^4\text{-}C_8H_8)(CO)_2(N_2)]$			2 022	
				1 975	
(8c)	$[Fe(\eta^2\text{-}C_8H_8)(CO)_3]$	2 037	2 035	2 041	2 039
		1 982[b]	1 987	1 998[b]	1 984[b]
		1 959	1 966	1 964	1 961
(8d)	$[Fe(\eta^2\text{-}C_8H_8)(CO)_4]$				2 021
					2 011
	$[Fe(CO)_5]$[p]				2 026
					2 002
					1 996
	$HCO^{\bullet}$				1 860

[a] Data from ref. 6 for complexes **(1)**, **(1a)**, **(1b)**, and **(1c)**. [b] Matrix-split band. [c] ν_{NN} at 2 209 cm^{-1}. [d] Coincident band with photoproduct in some cases. [e] Extended photolysis produced three further new bands assigned to $[Fe(\eta^4\text{-}C_4H_4)(CO)(N_2)_2]$ (ν_{NN} at 2 168 and 2 116, ν_{CO} at 1 998 cm^{-1}). [f] Split bands observed upon annealing and attributed to types of dinitrogen complex which have slightly different geometries: ν_{NN} at 2 208 and 2 205 cm^{-1}. [g] Data from photolysis of complex **(2)** in carbon monoxide matrices. [h] ν_{CO}(ketonic). [i] ν_{NN} at 2 226 cm^{-1}. [j] Other expected bands obscured by parent and major product bands. [k] ν_{NN} at 2 215 cm^{-1}. [l] Extended photolysis produced two further weak bands assigned to $[Fe(\eta^4\text{-}C_6H_8)(CO)(N_2)_2]$ (ν_{NN} at 2 100, ν_{CO} at 2 000 cm^{-1}). [m] ν_{NN} at 2 208 cm^{-1}. [n] ν_{NN} at 2 215 cm^{-1}. [o] ν_{NN} at 2 207 cm^{-1}. [p] Band positions vary slightly from experiment to experiment depending on which substrate the $[Fe(CO)_5]$ was derived from.

yet another complication in as much that two additional new bands appeared at 2 020 and 1 960 cm^{-1} while the bands for **(2d)** decreased in intensity [Figure 4(*g*)]. The species responsible for these additional bands may be designated **(2e)** which is likely to be closely related to **(2c)** and **(2d)**. Finally the bands for **(2e)** completely disappeared when the matrix was irradiated with visible light (filter D) and those due to **(2d)** increased in intensity [Figure 4(*h*)]; the bands of **(2e)** and **(2d)** grew and decreased alternately during cycles of annealing followed by photolysis followed by annealing.

The high dilution used (*ca.* 1:2 000–1:5 000) and the reversibility of the matrix reactions rule out the possibility that the new species are polynuclear complexes, *e.g.* $[Fe_2(C_8H_8)(CO)_6]$ **(2f)**. The terminal CO stretching band patterns for **(2c)**, **(2d)**, and **(2e)** are possibly consistent with $Fe(CO)_2$ fragments but this proposal can be ruled out because the new bands are at much higher wavenumbers than 'naked' $[Fe(\eta^4\text{-}C_4H_4)(CO)_2]$**(2a)** and even a matrix frequency shift corresponding to a $Fe(CO)_2$ ... matrix species, *cf.* $Fe(CO)_4$ ... matrix,[33] would not be sufficient to account for the high-wavenumber band positions. Another species which can be eliminated is naked $[Fe(CO)_3]$ (ν_{CO} at 2 040 and 1 930 cm^{-1}).[33] This species could conceivably have been formed by loss of the C_4H_4 ligand but the band pattern for $[Fe(CO)_3]$ does not correspond with any of those for **(2c)**, **(2d)**, or **(2e)**.

In view of the fact that complexes **(2c)** and **(2d)** were only formed by the radiation (filter B, 230 < λ < 390 nm) which could promote the forward and reverse processes (Scheme 1) it seems plausible to suggest that one or other of the species could have arisen from partial dechelation of the C_4H_4 ring, *i.e.* formation of $[Fe(\eta^2\text{-}C_4H_4)(CO)_3]$ analogously to the formation of $[Fe(\eta^2\text{-}C_4H_6)(CO)_3]$ **(1c)**. Normally, in order to ascertain the number of CO ligands in a $M(CO)_n$ fragment, experiments with ^{13}CO-doped matrices would be carried out in order to generate the full range of $[M(^{12}CO)_{n-m}(^{13}CO)_m]$ species. Such an approach was impossible for species **(2c)**, **(2d)**, and **(2e)** because the bands for the $M(^{12}CO)_n$ species overlap extensively.



Scheme 1. (*i*) 230 < λ < 280 nm; (*ii*) 320 < λ < 390 nm; (*iii*) λ > 420 nm; (*iv*) anneal to 35 K; (*v*) λ > 430 nm

Insights into the structure of **(2c)**, **(2d)**, and **(2e)** can be obtained from other complexes having polyenes bonded to transition metals. For example, the band positions of **(2c)** (ν_{CO}

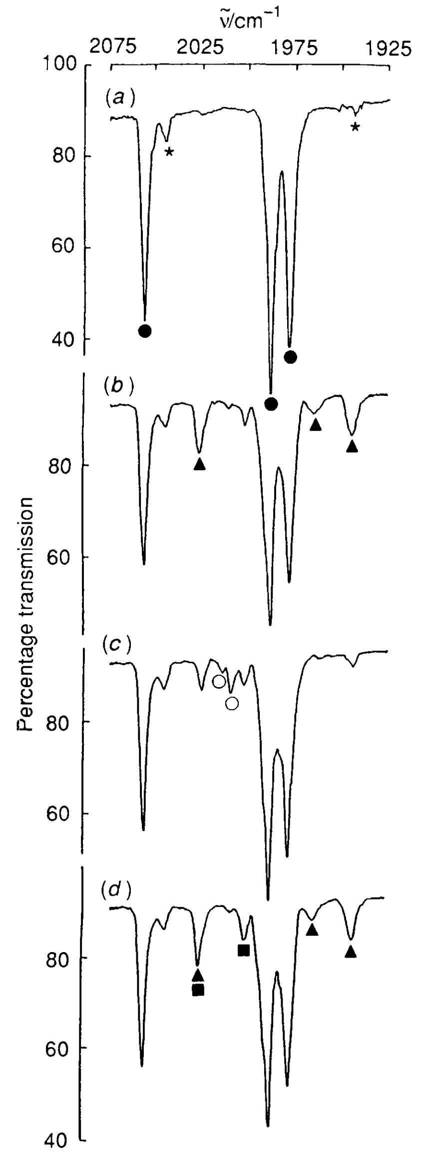


Figure 3. Infrared spectra from an experiment with $[Fe(\eta^4-C_4H_6)(CO)_3]$ (**1**) isolated in a carbon monoxide matrix at *ca.* 12 K (Grubb Parsons Spectromajor): (*a*) after deposition, (*b*) after 2 h of u.v. irradiation (filter A), (*c*) after a further 1 h of visible irradiation (filter D), and (*d*) after a further 15 min of u.v. irradiation (filter H). The asterisk indicates $[Fe(\eta^4-C_4H_6)(^{12}CO)_2(^{13}CO)]$ present in natural abundance; (●), (**1**); (▲), (**1c**); (○), (**1d**); (■), $[Fe(CO)_5]$

at 2 035 and 1 975 cm^{-1}) are very close to those of $[Fe(\eta^2-C_8H_8)(CO)_3]$ (ν_{CO} at 2 037, 1 982, and 1 959 cm^{-1})[9] and of $[Fe(\eta^2-C_2H_4)(CO)_3]$ (ν_{CO} at 2 039, 1 976, and 1 950 cm^{-1}).[6] On this basis (**2c**) may be proposed to be $[Fe(\eta^2-C_4H_4)(CO)_3]$ with an *s-cis* configuration (see Scheme 2). The band positions of (**2d**) and (**2e**) (ν_{CO} at 2 027, 1 968 and 2 020, 1 960 cm^{-1} respectively) are close to those of $[Fe(\eta^2$-*s-trans*-$C_4H_6)(CO)_3]$ (**1c**) (ν_{CO} at 2 024, 1 964, and 1 942 cm^{-1}) generated from (**1**) or from $[Fe(\eta^2-C_4H_6)(CO)_4]$.[6]

A transformation from a closed C_4H_4 ring to an open-ring system would not seem to be a process that could be reversed readily as demonstrated by the spectra in Figure 4. The fact that C_4H_4 moieties can co-ordinate with π- or σ-type bonding or a mixture of both in transition-metal complexes, and that CO can insert into the ring to give $[Fe(\eta^4-C_4H_4CO)(CO)_3]$[22] suggests that (**2d**) and (**2e**) may be metallocyclic complexes where the $Fe(CO)_3$ fragment is π- and σ-bonded to the ring (Scheme 2).

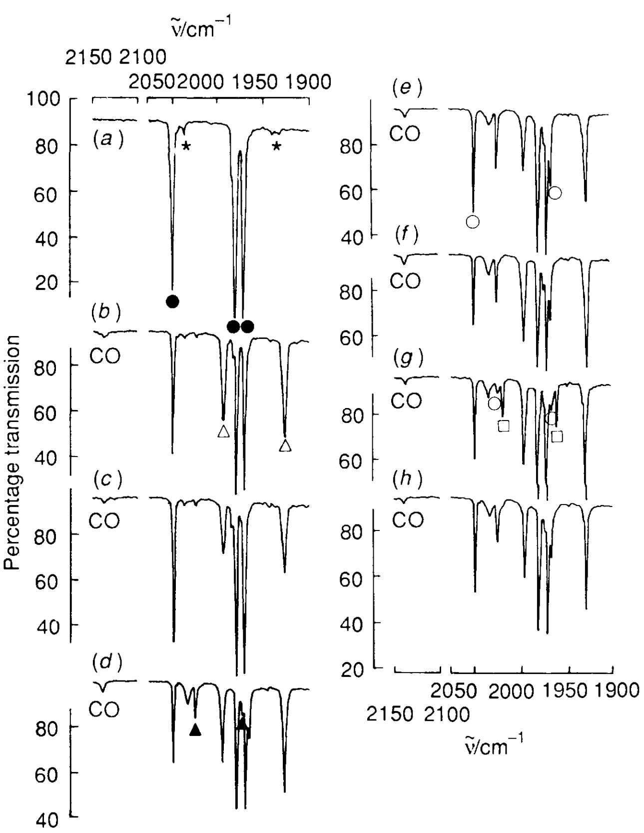
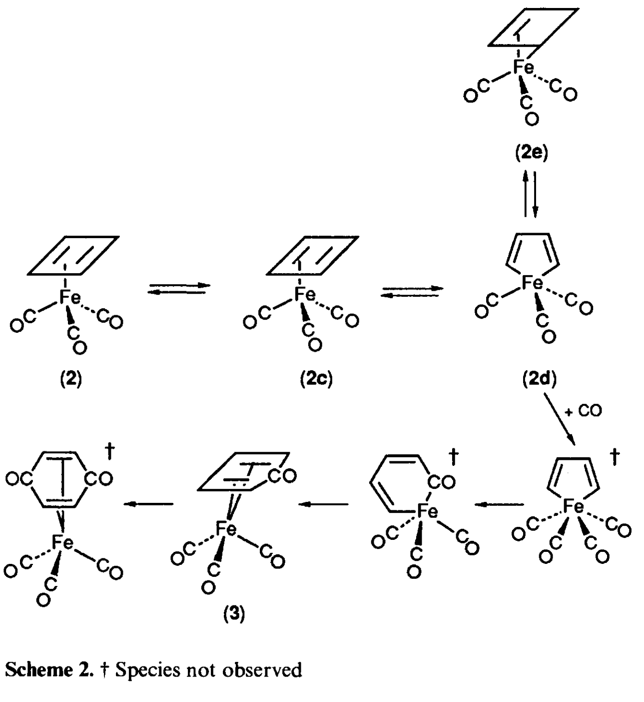
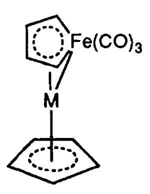


Figure 4. Infrared spectra from an experiment with $[Fe(\eta^4-C_4H_4)(CO)_3]$ (**2**) isolated in a methane matrix at *ca.* 12 K (Grubb Parsons Spectromajor): (*a*) after deposition, (*b*) after 2 h of u.v. irradiation (filter A), (*c*) after further 2 h of irradiation (filter C), (*d*) after a further 7 h of irradiation (filter B), (*e*) after a further 2 h of visible irradiation (filter D), (*f*) after a further 1 h of u.v. irradiation (filter A), (*g*) after annealing to *ca.* 35 K, and (*h*) after a further 1 h of visible irradiation (filter D). The asterisk indicates $[Fe(\eta^4-C_4H_4)(^{12}CO)_2(^{13}CO)]$ present in natural abundance; (●), (**2**); (△), (**2a**); (▲), (**2c**); (○), (**2d**); (□), (**2e**)



Scheme 2. † Species not observed

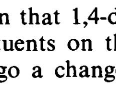


(2g)

Table 3. Observed and calculated[a] terminal CO-stretching bands (cm^{-1}) for [Fe(η^4-C_4H_4CO)(CO)$_3$] (**3**) and its photolysis products in ^{13}CO-doped (5%) matrices at *ca.* 12 K

Compound (symmetry point group)		Observed	Calculated
[Fe(η^4-C_4H_4CO)(^{12}CO)$_3$] (**3**)	A'	2 081.6	2 082.0
(C_s)	A'	2 022.4	2 023.1
	A''	2 001.5	2 001.9
[Fe(η^4-C_4H_4CO)(^{12}CO)$_2$(^{13}CO)][b]	A'	2 067.4	2 067.1
(C_s)	A''	2 000.3	2 000.9
	A'	1 993.1	1 992.4
[Fe(η^4-C_4H_4CO)(^{12}CO)$_2$(^{13}CO)][c]	A	2 074.4	2 074.2
(C_1)	A	2 015.6	2 017.9
	A	*d*	1 968.8
[Fe(η^4-C_4H_4CO)(^{12}CO)(^{13}CO)$_2$][e]	A	2 005.2	2 054.5
(C_1)	A	1 993.1	1 994.1
	A	1 965.7	1 966.8
[Fe(η^4-C_4H_4CO)(^{12}CO)(^{13}CO)$_2$][f]	A'	2 067.4	2 066.3
(C_s)	A'	1 993.1	1 993.2
	A''	1 956.2	1 956.4
[Fe(η^4-C_4H_4CO)(^{13}CO)$_3$]	A'	*g*	2 035.7
(C_s)	A'	*d*	1 978.2
	A''	1 956.2	1 956.4
[Fe(η^4-C_4H_4CO)(^{12}CO)$_2$] (**3a**)	A_1	2 032.3	2 031.4
(C_{2v})	B_1	1 975.3	1 975.6
[Fe(η^4-C_4H_4CO)(^{12}CO)(^{13}CO)]	A'	2 016.6	2 017.4
(C_s)	A''	1 946.3	1 945.6
[Fe(η^4-C_4H_4CO)(^{13}CO)$_2$]	A_1	1 987.7	1 986.2
(C_{2v})	B_1	1 930.5	1 931.7

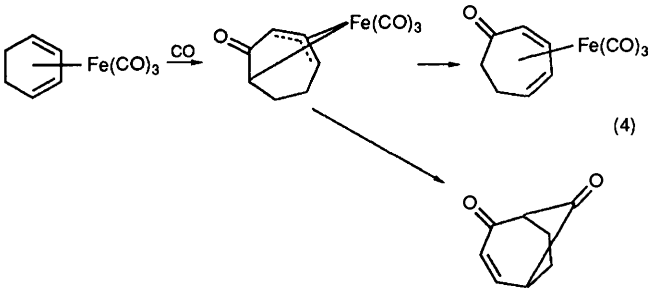
[a] Refined energy-factored force-field constants (N m^{-1}) defined by the numbering below are: for [Fe(η^4-C_4H_4CO)(CO)$_3$], K_1 = 1 701.3, K_2 =



$1 \neq 2 = 3$

K_3 = 1 660.5, $k_{12} = k_{13}$ = 34.5, k_{23} = 43.0; for [Fe(η^4-C_4H_4CO)$_2$], K = 1 622.0, k_i = 45.1. [b] ^{13}CO in position 1. [c] ^{13}CO in position 2. [d] Band obscured by overlap. [e] ^{12}CO in position 2. [f] ^{12}CO in position 1. [g] Band obscured by matrix band.

Support for such $\pi \rightleftarrows \sigma$ interconversion has been afforded by the observation that 1,4-diazabuta-1,3-diene (dab) ligands containing substituents on the N atoms, which are not too bulky, can undergo a changeover from σ,σ-N,N′ to π,π co-ordination in [Fe(CO)$_3$(dab)] if these complexes are irradiated in argon or carbon monoxide matrices at 10 K.[34] Annealing the matrix to *ca.* 35 K may have induced (**2d**) to (**2e**) interconversion *via* $\pi \longrightarrow \sigma$ rearrangement (Scheme 2); (**2e**) could revert to (**2d**) on irradiation. Complexes with metallocycle features have been proposed a long time ago[35] and recently the structures of the metallametallocene complexes, [M(η^5-C_5H_5){C_4H_4Fe(CO)$_3$}] (**2g**; M = Co or Rh), have been determined by *X*-ray crystallography.[36] These complexes have terminal CO-stretching bands at 2 035 and 1 965 cm^{-1}. A complex of the type η^3-σ-diene iron tricarbonyl [*cf.* (**2e**)] has also been identified and proposed[37] to be involved in a reaction of CO insertion into the ring of [Fe(η^4-C_6H_8)(CO)$_3$] to form [Fe(η^4-C_6H_8CO)(CO)$_3$] [equation (4)]. Analogous experiments were carried out with (**2**) isolated at high dilutions in argon matrices (Table 2). In this case the relative amount of (**2c**) was greater than that of (**2d**) and the photochemical reactions were slower.



(4)

(*v*) *Photolysis of* [Fe(η^4-C_4H_4CO)(CO)$_3$] (**3**) *in* ^{13}*CO-doped methane gas matrices at* ca. 12 K. In a ^{13}CO-doped methane matrix irradiation (filter B) of complex (**3**) led to facile ^{12}CO–^{13}CO exchange for the Fe(CO)$_3$ fragment but no exchange for the ketonic CO group. This is consistent with the failure to effect ketonic CO ring-to-metal transfer in argon, methane, and carbon monoxide matrices (see above). Fitting of the observed and calculated[38,39] bands for a C_s Fe(CO)$_3$ fragment gave good agreement (Table 3) and a satisfactory correspondence with the ^{12}CO–^{13}CO photoproduct bands first assigned to (**3**) when (**2**) was photolysed in mixed ^{12}CO–^{13}CO matrices.[22]

(*b*) *Photolysis of* [Fe(η^4-C_5H_6)(CO)$_3$] (**4**) *and* [Fe(η^4-C_7H_{10})(CO)$_3$] (**6**) *in Frozen Gas Matrices at* ca. 12 K.—(*i*) *Argon and methane matrices.* Photolysis with u.v. irradiation (filter H) of a methane matrix containing [Fe(η^4-C_7H_{10})(CO)$_3$] isolated at high dilution (1:2 000—1:5 000) at *ca.* 12 K [Figure 5(*a*), Table 2] resulted in the appearance of seven new bands at 2 138 ('free' CO), 2 047, 1 994, 1 992, 1 979, 1 930, and 1 927 cm^{-1} at the expense of the parent bands [Figure 5(*b*)]. In view of the CO expulsion and the similarity of the band pattern of the bands marked △ to those of other co-ordinatively unsaturated 16-electron species [Fe(η^4-polyene)(CO)$_2$] (see above, Table 2) and that of [Fe(η^4-$C_5H_4Me_2$)(CO)$_2$] (ν_{CO} at 1 995 and 1 931 cm^{-1} in Ar)[10] it seems reasonable to assign the bands at 1 994, 1 992, 1 930, and 1 927 cm^{-1} to [Fe(η^4-C_7H_{10})(CO)$_2$] (see below for a discussion of doublet patterns). The appearance of other new bands (marked ■) at slightly higher wavenumbers than those of [Fe(η^4-C_7H_{10})(CO)$_3$], observed initially, could be taken to indicate the formation of a tricarbonyl species with the ring adopting a higher-energy conformation, *cf.* the 'tub' $\rightleftarrows$ 'chair' isomerisation of [Fe(η^4-C_8H_8)(CO)$_3$].[9] The fact that these new bands are already apparent as shoulders on the bands after deposition [Figure 5(*a*)] is suggestive of another possibility, namely that an equilibrium process exists in the gas phase which can be quenched at the cold window and that this equilibrium can be perturbed photochemically in matrices at 12 K. An energetically feasible process is a flip of the saturated carbons downwards so that H_{endo} becomes closer to the metal as illustrated in Scheme 3. A small interaction from H_{endo}, which is consistent with the now widely recognised agostic interactions,[40] will increase the electron density at the metal with a resultant increase in the back donation (Fe→C) and a decrease in the C–O bond order, *i.e.* bands will move to lower wavenumbers. The bands at higher wavenumbers (2 047 and 1 979 cm^{-1}) can, therefore, probably be assigned to the 'non-interacting' conformer (**6**) while those at lower wavenumbers (2 045, 1 977, 1 976, and 1 970 cm^{-1}) may be assigned to the 'interacting' conformer (**6′**). It is interesting that the intensity ratio (**6**):(**6′**) rises to approximately 1:0.8 (on the basis of the bands at 2 047 and 2 045 cm^{-1}) and then remains constant upon prolonged photolysis, however the bands for (**6′**) at 1 977 and 1 976 cm^{-1}

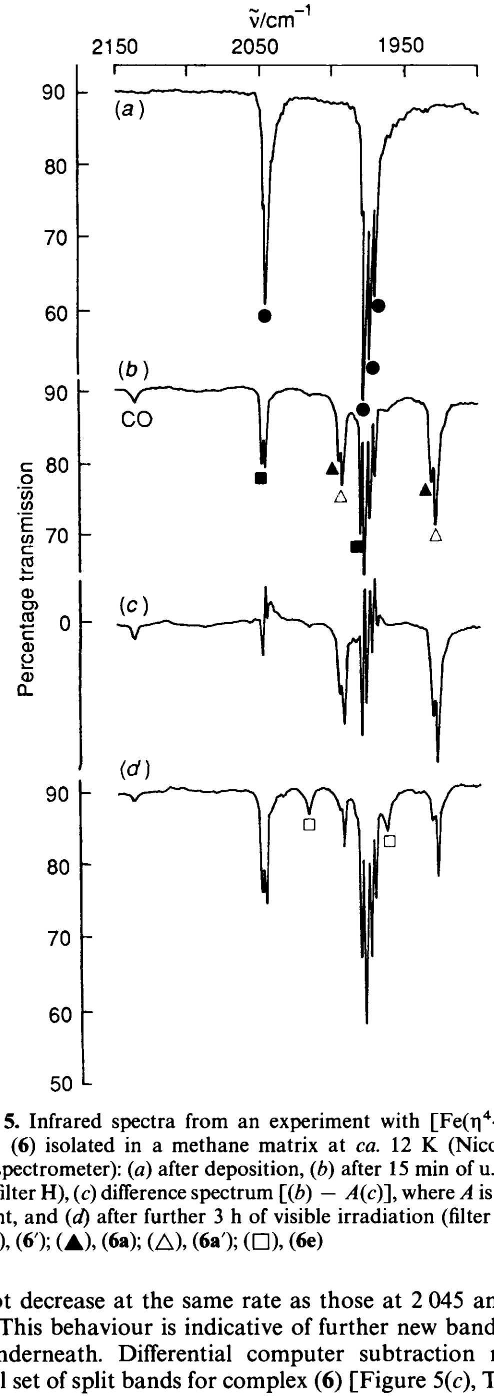
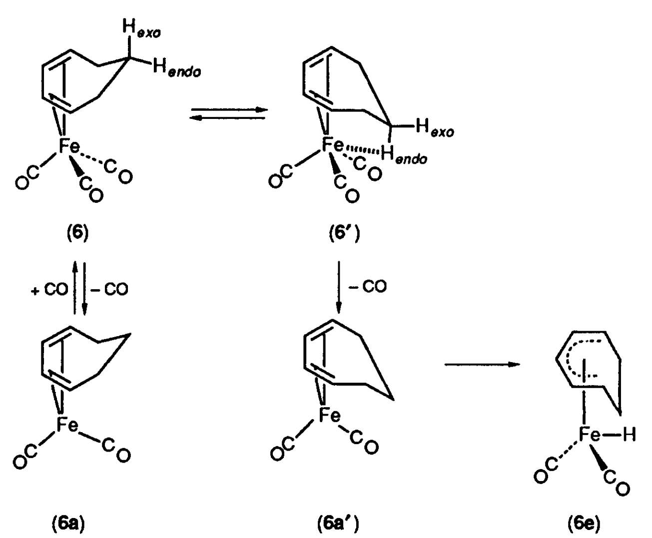


Figure 5. Infrared spectra from an experiment with $[Fe(\eta^4-C_7H_{10})(CO)_3]$ (**6**) isolated in a methane matrix at *ca.* 12 K (Nicolet 7199 FTIR spectrometer): (*a*) after deposition, (*b*) after 15 min of u.v. irradiation (filter H), (*c*) difference spectrum [(*b*) − *A*(*c*)], where *A* is a scaling constant, and (*d*) after further 3 h of visible irradiation (filter D). (■), (**6**); (●), (**6′**); (▲), (**6a**); (△), (**6a′**); (□), (**6e**)

did not decrease at the same rate as those at 2 045 and 1 970 cm^{-1}. This behaviour is indicative of further new bands growing underneath. Differential computer subtraction revealed the full set of split bands for complex (**6**) [Figure 5(*c*), Table 2]. A similar 'non-interacting' and 'interacting' pair of conformers is expected for the 16-electron co-ordinatively unsaturated species $[Fe(\eta^4-C_7H_{10})(CO)_2]$ described above, *i.e.* bands at 1 994 and 1 930 cm^{-1} are due to (**6a**) and bands at 1 992 and 1 927 cm^{-1} are due to (**6a′**) as shown in Scheme 3. On further photolysis with visible radiation (filter D) the bands due to (**6a**) and (**6a′**) decreased in intensity, a small increase was observed for (**6**), and gradually two further bands grew at 2 016 and 1 961 cm^{-1} [Figure 5(*d*)]. By comparison with the bands of $[Fe(\eta^5-C_5H_4Me)(CO)_2H]$ (ν_{CO} at 2 014 and 1 958 cm^{-1} in Ar)[10] and $[Fe(\eta^5-C_5H_5)(CO)_2H]$ (ν_{CO} at 2 026 and 1 971 cm^{-1} in Ar),[10,41]



Scheme 3.

the new bands may be attributed to $[Fe(\eta^5-C_7H_9)(CO)_2H]$ (**6e**). The pattern of increasing and decreasing photoproduct bands in this photolysis suggests that (**6a**) reverts to (**6**) by recapturing an ejected CO and that (**6a′**) forms the dicarbonylhydrido species (**6e**) *via* H_{endo} migration from the ring to the metal (Scheme 3).* Analogous observations were recorded in an argon matrix (Table 2) although the photoreaction rate was slower.

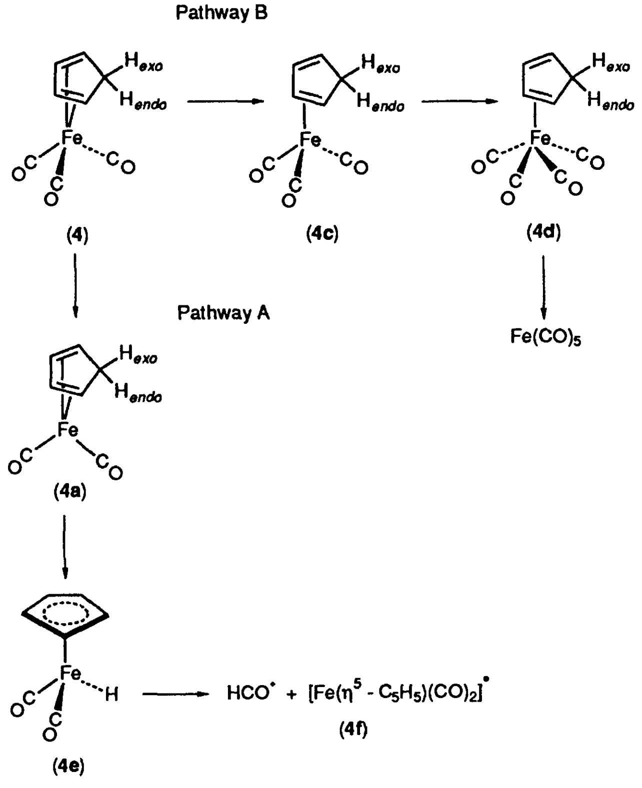
In the case of $[Fe(\eta^4-C_5H_6)(CO)_3]$ (**4**) the ring system would appear not to be large enough to interact with the iron centre by puckering as with (**6**). Nevertheless, once CO ejection to form $[Fe(\eta^4-C_5H_6)(CO)_2]$ (**4a**) had taken place then H transfer efficiently occurred to yield $[Fe(\eta^5-C_5H_5)(CO)_2H]$ (**4e**), *cf.* the formation of $[Fe(\eta^4-C_5H_4Me_2)(CO)_2]$ (ν_{CO} at 1 995 and 1 931 cm^{-1} in Ar) and ultimately $[Fe(\eta^5-C_5H_4Me)(CO)_2Me]$ on photolysis of $[Fe(\eta^5-C_5H_4Me_2)(CO)_3]$ at 10 K.[10]

(*ii*) *Nitrogen matrices.* Photolysis of $[Fe(\eta^4-C_7H_{10})(CO)_3]$ (**6**) shows photoreactions which are similar to those of other $[Fe(\eta^4\text{-polyene})(CO)_3]$ complexes, *viz.* conformers of (**6**) were produced and CO substitution occurred to yield $[Fe(\eta^4-C_7H_{10})(CO)_2(N_2)]$ (**6b**) (Table 2) on u.v. irradiation (filter H). Further visible irradiation (filter D) or annealing the matrix to *ca.* 30 K resulted in no significant changes in the i.r. spectra.

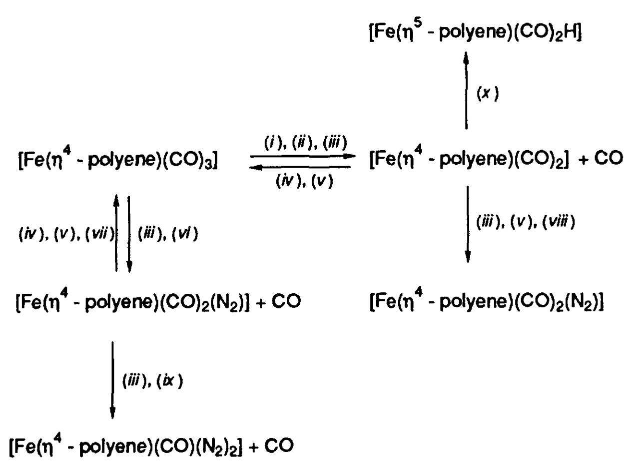
(*iii*) *Carbon monoxide matrices.* Photolysis (filter A, 130 min) of $[Fe(\eta^4-C_5H_6)(CO)_3]$ (**4**) in a CO matrix (ν_{CO} at 2 050, 1 982, and 1 974 cm^{-1}) produced two bands at 2 025 and 1 967 cm^{-1} which may be assigned to $[Fe(\eta^5-C_5H_5)(CO)_2H]$ (**4e**) (see above). Irradiation with long-wavelength light (filter D), however, failed to yield the unsaturated species (**4a**) seen in methane matrices. A combination of high- and low-energy light (filter H, 30 min) gave new weak bands at 2 038 and 2 004 cm^{-1} which grew on further combined-wavelength irradiation (filter H, 60 min) but did not grow when visible light (filter D) was used. Bands were now clearly visible at 2 038, 2 004, 1 997, 1 956, 1 940, and 1 860 cm^{-1}. A subtraction spectrum at this stage, with bands for (**4**) ratioed out, revealed further bands at 2 040, 2 027, 2 024, 1 966, and 1 962 cm^{-1} of which the band at 1 966 cm^{-1} is not due to $[Fe(\eta^5-C_5H_5)(CO)_2H]$ (ν_{CO} at 1 967 cm^{-1}). On photolysis with a different high- and low-energy source (filter F, 65 min) bands due to the species (**4**) and (**4e**) decreased while all the other bands increased; the bands at 2 027 and 1 962 cm^{-1} became clearly visible. A final irradiation with long-wavelength light (filter E, 70 min) produced little change except broadening was observed in the parent band of (**4**) at 1 983 cm^{-1}, *i.e.* there may be a hidden band at *ca.* 1 982 cm^{-1}. Annealing resulted in a decrease in the band at 1 967 cm^{-1} and

---

* Another instance of H_{endo}-to-metal migration, which occurs in the gas phase and is only detected by quenching the species, is the equilibrium between $[Mo(\eta^5-C_7H_8)(CO)_3]$ and $[Mo(\eta^7-C_7H_7)(CO)_3H]$.[42]



Scheme 4.



Scheme 5. (*i*) Complexes (**1**)—(**4**), CH_4 or Ar; (*ii*) (**5**); CH_4, Ar, CO, or N_2; (*iii*) u.v. radiation; (*iv*) visible radiation; (*v*) annealing; (*vi*) (**1**)—(**4**), N_2; (*vii*) (**3**), N_2; (*viii*) (**5**), N_2; (*ix*) (**2**), N_2; (*x*) (**4**), (**6**); CH_4 or Ar

the appearance of a clear peak at 1 960 cm^{-1} while the two distinct bands could be seen at 2 027 and 2 024 cm^{-1}.

In order to explain the observation of so many new bands it is necessary to consider the possible reaction pathways (A and B, Scheme 4). Evidence in support of pathway A comes from the initial observation of the formation of complex (**4e**) (ν_{CO} at 2 025 and 1 967 cm^{-1}) and the later observation of a band at 1 860 cm^{-1} which may be assigned to the radical $HCO^{\bullet}$ (ν_{CO} at 1 860 cm^{-1}).[43] The latter reaction is analogous to the formation of $[M(\eta^5\text{-}C_5H_5)(CO)_3]^{\bullet}$ (M = Mo or W) and $HCO^{\bullet}$ radicals on photolysing $[M(\eta^5\text{-}C_5H_5)(CO)_3H]$ (M = Mo or W) complexes in carbon monoxide matrices.[44]

The precedent for pathway B comes from the photolysis of $[Fe(\eta^4\text{-}C_4H_6)(CO)_3]$ (**1**) (ν_{CO} at 2 057, 1 989, and 1 979 cm^{-1}) in carbon monoxide matrices when $[Fe(\eta^2\text{-}C_4H_6)(CO)_3]$ (**1c**) (ν_{CO} at 2 026, 1 965, and 1 944 cm^{-1}) and $[Fe(\eta^2\text{-}C_4H_6)(CO)_4]$ (**1d**) (ν_{CO} at 2 014 and 2 009 cm^{-1}) were proposed to be formed.[6] Support from the latter came from a separate experiment on an authentic sample of $[Fe(\eta^2\text{-}C_4H_6)(CO)_4]$ (ν_{CO} at 2 088m, 2 018m, 2 008vs, and 1 988vs cm^{-1})[6] where the bands at 2 088 and 1 988 cm^{-1} are obscured by matrix ^{13}CO and parent (**1**), respectively.

On the basis of these results it is possible to assign the bands at 2 004 and 1 997 cm^{-1} to $[Fe(\eta^2\text{-}C_5H_6)(CO)_4]$ (**4d**). The similarity, apart from the shift to lower wavenumbers, of the set of bands at 2 038, 1 962, and 1 953 cm^{-1} to those of the parent (**4**) and the relative shift between (**1**) and (**1c**) suggests that the species responsible for them is $[Fe(\eta^2\text{-}C_5H_6)(CO)_3]$ (**4c**). The final product in pathway B is total dechelation of the diene to yield C_5H_6 and $[Fe(CO)_5]$ of which the latter is identified (Table 2) *via* the bands at 2 027 and 2 003 cm^{-1}, partially obscured by the band of (**4d**) at 2 004 cm^{-1}.

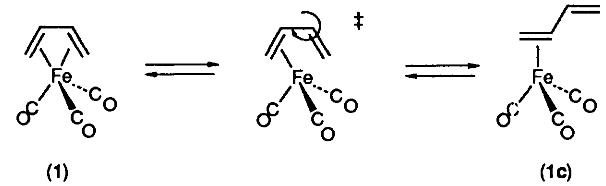
The remaining bands, which are all weak, appeared after an extensive period of u.v. irradiation and therefore they probably arise from secondary photolysis. A recent time-resolved study of $[\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$ has assigned terminal CO stretching bands at 2 004 and 1 938 cm^{-1} (cyclohexane) to the very short-lived radical $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^{\bullet}$.[45] The relative intensities of the two bands at 2 004 and 1 938 cm^{-1} is approximately 1:2,[45] such that, in the case of overlapping bands, the band at 2 004 cm^{-1} might be obscured by bands due to other more abundant species, *e.g.* those arising from $[Fe(\eta^5\text{-}C_5H_5)(CO)_2H]$ and $[Fe(\eta^2\text{-}C_5H_6)(CO)_4]$ (2 020s and 2 004m cm^{-1} respectively, Table 2). The weak band at 1 940 cm^{-1} can, however, be reasonably correlated with the band for the radical (**4f**) at 1 930 cm^{-1} in cyclohexane solutions, in accordance with path A in Scheme 4.

In carbon monoxide matrices, where the bands of $[Fe(\eta^4\text{-}C_7H_{10})(CO)_3]$ (**6**) are broader at the outset, initial u.v. photolysis (filter H) led to further band broadening rather than clearly resolved peaks. Computer subtraction, however, revealed the presence of the other conformer (**6′**) growing in. Extended u.v. photolysis (filter H) gave new bands which may be assigned to $[Fe(CO)_5]$ (ν_{CO} at 2 027, 2 003, and 1 996 cm^{-1}) by analogy with the photoreactions of (**1**) and (**8**). Surprisingly there was no evidence for bands which could be attributed to $[Fe(\eta^2\text{-}C_7H_{10})(CO)_4]$ or any other intermediate ring-dissociation products.

Discussion

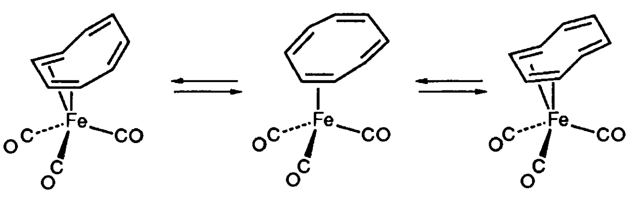
The range of possible photoreactions for $[Fe(\eta^4\text{-polyene})(CO)_3]$ complexes (Scheme 5) will depend on the energy of the radiation used. The electronic spectra of such complexes show very strong absorption bands below 260 nm with one or two medium-intensity bands at *ca.* 330 nm (Table 1). Both types of absorption are in the u.v. region of the spectrum so it is not surprising that irradiation with u.v. light causes photoreactions. The former strong bands have been assigned to charge-transfer metal-to-ligand $[M \longrightarrow \pi^*(CO)]$ transitions[17] while the latter medium-intensity bands are assigned as ligand-field (*d–d*) absorption bands. Forward photolysis invariably required irradiation with u.v. light, *i.e.* 230—300 nm (filters A, B, and H), which suggests that the excited states, $[Fe(\eta^4\text{-polyene})(CO)_3]^*$, populated by irradiation are $M \longrightarrow \pi^*(CO)$ excited states. Population of such excited states leads to M–C(O) bond weakening and dissociation of CO ligand as is observed for the primary photoprocess (Scheme 5).

The observation of the 16-electron co-ordinatively unsaturated $[Fe(\eta^4\text{-polyene})(CO)_2]$ species in gas matrices is consistent with the proposals for a CO-dissociative pathway as the primary process in the photochemistry of the $[Fe(\eta^4\text{-polyene})(CO)_3]$ complexes in solution.[11–21] The reactivity of



(1) (1c)

Scheme 6. ‡ Species not observed



(8) (8c) (8′)

Scheme 7.

the $[\mathrm{Fe}(\eta^4\text{-polyene})(\mathrm{CO})_2]$ fragments is demonstrated by recombination with the ejected CO ligand, which is trapped locally in the matrix, and the reaction with N_2 to give $[\mathrm{Fe}(\eta^4\text{-polyene})(\mathrm{CO})_2(\mathrm{N}_2)]$ complexes when matrices containing $[\mathrm{Fe}(\eta^4\text{-polyene})(\mathrm{CO})_2]$ are annealed to *ca.* 35 K, *i.e.* a thermal reaction, or irradiated with visible light. The observation of 'naked' $[\mathrm{Fe}(\eta^4\text{-}\mathrm{C_8H_8})(\mathrm{CO})_2]$ species in nitrogen and carbon monoxide matrices may be taken to indicate stabilisation of the 16-electron fragment by additional interaction with the uncomplexed double bonds of the C_8H_8 ring. It is not yet clear why such an interaction does not lead to further new 18-electron species, *i.e.* $[\mathrm{Fe}(\eta^6\text{-}\mathrm{C_8H_8})(\mathrm{CO})_2]$ and $[\mathrm{Fe}(\eta^8\text{-}\mathrm{C_8H_8})(\mathrm{CO})]$; such a stepwise sequence is observed for $[\mathrm{Mn}(\sigma\text{-}\mathrm{C_7H_7})(\mathrm{CO})_5]$ in gas matrices at 12 K.[46] It is interesting in this latter case that the decarbonylation species observed are all 18-electron species, *viz.* $[\mathrm{Mn}(\eta^3\text{-}\mathrm{C_7H_7})(\mathrm{CO})_4]$, $[\mathrm{Mn}(\eta^5\text{-}\mathrm{C_7H_7})(\mathrm{CO})_3]$, and $[\mathrm{Mn}(\eta^7\text{-}\mathrm{C_7H_7})(\mathrm{CO})_2]$, rather than 16-electron species, *e.g.* $[\mathrm{Mn}(\sigma\text{-}\mathrm{C_7H_7})(\mathrm{CO})_4]$.

Although the CO-dissociation path is probably the most important photochemical reaction path other paths involving the polyene ligand should not be discounted. For example, i.r. spectroscopy in gas matrices has characterised at least two new types of η^2-diene–iron co-ordination, *e.g.* an *s-cis* configuration for $[\mathrm{Fe}(\eta^2\text{-}\mathrm{C_4H_4})(\mathrm{CO})_3]$ and for $[\mathrm{Fe}(\eta^2\text{-}\mathrm{C_8H_8})(\mathrm{CO})_3]$, and an *s-trans* configuration for $[\mathrm{Fe}(\eta^2\text{-}\mathrm{C_4H_6})(\mathrm{CO})_3]$. The η^2-ring binding was supported by the observation of $[\mathrm{Fe}(\eta^2\text{-}\mathrm{C_4H_6})(\mathrm{CO})_4]$, $[\mathrm{Fe}(\eta^2\text{-}\mathrm{C_8H_8})(\mathrm{CO})_4]$, and ultimately $[\mathrm{Fe}(\mathrm{CO})_5]$ when (**1**) and (**8**) were irradiated in carbon monoxide matrices respectively. The failure to observe a species with an *s-cis* configuration on photolysis of (**1**) is probably due to instantaneous isomerisation (Scheme 6) upon irradiation and that the reverse reaction cannot occur thermally, *i.e.* by annealing at cryogenic temperatures. As discussed previously,[9] it is possible that the $[\mathrm{Fe}(\eta^2\text{-}\mathrm{C_8H_8})(\mathrm{CO})_3]$ species could be an intermediate in the 'tub'-$C_8H_8 \rightleftharpoons$ 'chair'-C_8H_8 conformational interconversion (Scheme 7). The additional photoreactions of $[\mathrm{Fe}(\eta^4\text{-}\mathrm{C_4H_4})(\mathrm{CO})_3]$ (**2**) are very different from those of (**1**) and (**5**) because of the possibility of $\pi \rightleftharpoons \sigma$ rearrangement leading to formation of a metallocycle. Metallocyclopentadiene structures have been proposed for complexes with Ti,[47] Zr,[48] Fe,[35,36,49] Os,[50] Mn,[51] Co,[14] Ir,[52] and Rh[52,53] and several such structures have been substantiated by *X*-ray crystallography.[36,54] One of the three mechanisms for rearrangement from an olefin complex is *via* an intermediate metallocycle formation in which pairwise exchange between two olefins occurs. Analysis[55] of the frontier orbitals and photoelectron spectra of (**2**) indicates that the molecule is better described as a $\mathrm{Fe}(\mathrm{C_4H_4})$ fragment perturbed by three CO ligands rather than as a $\mathrm{Fe}(\mathrm{CO})_3$ fragment perturbed by a C_4H_4 ring. Additionally, it has been discovered that the Fe–C_4H_4 bond is highly covalent with six electrons delocalised into metal–ring π orbitals; a phenomenon referred to as metalloaromaticity. In order to form a metallocycle it was suggested[56] that since the metal contributes no π electrons but offers vacant *p* and *d* orbitals then the π electrons of the diene can be delocalised in Hückel–Mobius orbitals.[57] This set of requirements could be achieved for (**2**) as a result of initial de-carbonylation. The $\pi \rightleftharpoons \sigma$ isomerisation could then occur as the species takes up thermal energy (annealing) or photochemical energy (long-wavelength radiation). Support for the proposed metallocyclic species [(**2c**), (**2d**), and (**2e**)] is afforded by the identification of $[\mathrm{Fe}(\eta^4\text{-}\mathrm{C_4H_4CO})(\mathrm{CO})_3]$ (**3**) on photolysis of (**2**) in carbon monoxide matrices. A possible pathway for the formation of complex (**3**) is given in Scheme 2. It is interesting that further insertion of CO into the cyclopentadienone ring of (**3**) did not take place.

Evidence for the formation of species with additional CO ligands, *i.e.* $[\mathrm{Fe}(\eta^2\text{-polyene})(\mathrm{CO})_4]$ and $[\mathrm{Fe}(\mathrm{CO})_5]$, suggests that polyene ejection can take place (Scheme 8). This has been observed both thermally and photochemically in solution for (**1**) and (**5**).[11,15,20,21] Ejection has been claimed for C_4H_4 from (**2**) in gas-phase studies[58] but studies of relative quantum yields ($\varphi_{C_4H_4}:\varphi_{CO} < 1:10$) and the work in matrices suggests the gas-phase claim was mistaken.

$$\begin{tikzcd}
{[\mathrm{Fe}(\eta^4\text{-polyene})(\mathrm{CO})_3]} \arrow[r] & {[\mathrm{Fe}(\eta^2\text{-polyene})(\mathrm{CO})_3]} \arrow[d, "+\mathrm{CO}"] \\
\text{polyene} + {[\mathrm{Fe}(\mathrm{CO})_5]} & {[\mathrm{Fe}(\eta^2\text{-polyene})(\mathrm{CO})_4]} \arrow[l, "+\mathrm{CO}"']
\end{tikzcd}$$

Scheme 8.

Hydrogen and alkyl migration from a polyene ring to metal are not unknown in iron carbonyl complexes. The formation of $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_7H_9})(\mathrm{CO})_2\mathrm{H}]$ is probably facilitated by the availability of H_{endo} very close to the metal as a result of (**6**) $\rightleftharpoons$ (**6′**) isomerisation and the creation of the vacant site by CO ejection (Scheme 4). That this process occurs even in carbon monoxide matrices and no $[\mathrm{Fe}(\eta^2\text{-}\mathrm{C_7H_{10}})(\mathrm{CO})_4]$ is formed underlines the importance of the $M \cdots H_{endo}$ interactions.

Acknowledgements

We thank Dr. F-W. Grevels for gifts of $[\mathrm{Fe}(\eta^4\text{-}\mathrm{C_4H_4CO})(\mathrm{CO})_3]$ and $[\mathrm{Fe}(\eta^4\text{-}\mathrm{C_8H_8})(\mathrm{CO})_3]$, Dr. N. Connelly for a gift of $[\mathrm{Fe}(\eta^4\text{-}\mathrm{C_4H_4})(\mathrm{CO})_3]$, the Universiti Teknologi Malaysia for Study Leave (to R. B. H.), and the S.E.R.C for support (to A. J. R.). We are grateful for the contributions of Drs. R. Narayanaswamy and D. J. Taylor at the early stages of this work. We also thank the referees for their helpful and constructive comments.

References

1 B. Dickens and W. N. Lipscombe, *J. Am. Chem. Soc.*, 1961, **83**, 489; *J. Chem. Phys.*, 1962, **37**, 2087.
2 E. A. Koerner von Gustorf, F-W. Grevels, and I. Fischler (editors), 'The Organic Chemistry of Iron,' Academic Press, London, 1978, vol. 1; *ibid.*, vol. 2; 1981, vol. 2.
3 A. J. Barnes, R. Gaufrès, A. Müller, and W. J. Orville-Thomas (editors), 'Matrix Isolation Spectroscopy,' NATO Advanced Study Institute Series, D. Reidel, Dordrecht, 1981.
4 A. J. Rest, in 'Matrix Isolation Spectroscopy', eds. A. J. Barnes, R. Gaufrès, A. Müller, and W. J. Orville-Thomas, NATO Advanced Study Institute Series, D. Reidel, Dordrecht, 1981, ch. 9.

5 R. B. Hitam, K. A. Mahmoud, and A. J. Rest, *Coord. Chem. Rev.*, 1984, **55**, 1; R. N. Perutz, *Chem. Rev.*, 1985, **85**, 77.

6 G. Ellerhorst, W. Gerhartz, and F-W. Grevels, *Inorg. Chem.*, 1980, **19**, 67.

7 O. L. Chapman, J. Pacansky, and P. W. Wojtkowski, *J. Chem. Soc., Chem. Commun.*, 1973, 681.

8 A. J. Rest, J. R. Sodeau, and D. J. Taylor, *J. Chem. Soc., Dalton Trans.*, 1978, 651.

9 R. B. Hitam, R. Narayanaswamy, and A. J. Rest, *J. Chem. Soc., Dalton Trans.*, 1983, 1351.

10 W. Gerhartz, G. Ellerhorst, P. Dahler, and P. Eilbracht, *Liebigs Ann. Chem.*, 1980, 1296.

11 J. Schwartz, *J. Chem. Soc., Chem. Commun.*, 1972, 814.

12 F. M. Chaudhari and P. L. Pauson, *J. Organomet. Chem.*, 1966, **5**, 73.

13 F. Faraone, F. Zingales, P. Ugnayliati, and U. Belluco, *Inorg. Chem.*, 1968, **7**, 2362.

14 N. G. Connnelly, R. L. Kelly, M. O. Kitchen, R. M. Mills, R. F. D. Standfield, M. W. Whiteley, S. Whiting, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1981, 1317.

15 G. N. Schrauzer and P. Glockner, *J. Am. Chem. Soc.*, 1968, **90**, 2800.

16 T. H. Whitesides and J. Shelly, *J. Organomet. Chem.*, 1975, **92**, 215.

17 M. S. Wrighton, *Chem. Rev.*, 1974, **74**, 401; G. L. Geoffroy and M. S. Wrighton, 'Organometallic Photochemistry,' Academic Press, London, 1979.

18 P. Reeves, J. Henery, and R. Pettit, *J. Am. Chem. Soc.*, 1969, **91**, 5888.

19 I. Fischler, K. Hildenbrand, and E. A. Koerner von Gustorf, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 54.

20 O Jaenicke, R. C. Kerber, P. Kirsch, and E. A. Koerner von Gustorf, *J. Organomet. Chem.*, 1980, **187**, 361.

21 W. Strohmeier, *Angew. Chem., Int. Ed. Engl.*, 1964, **3**, 730.

22 A. J. Rest and D. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 1981, 489.

23 R. B. Hitam, Ph.D. Thesis, University of Southampton, 1984.

24 R. K. Kochler and R. Pettit, *J. Organomet. Chem.*, 1966, **6**, 272.

25 A. Birch, P. Cross, J. Lewis, D. White, and S. Wild, *J. Chem. Soc. A*, 1968, 332.

26 R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1961, 594; H. J. Dauben, jun., and D. J. Bartelli, *J. Am. Chem. Soc.*, 1961, **83**, 497; M. Brookhart, K. J. Karel, and L. E. Nance, *J. Organomet. Chem.*, 1977, **140**, 203.

27 A. J. Deeming, S. Ullah, A. Domingos, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1974, 203.

28 M. M. Rochkind, *Spectrochim. Acta, Part A*, 1971, **27**, 547.

29 D. C. Andrews and G. Davidson, *J. Organomet. Chem.*, 1974, **76**, 373.

30 D. C. Andrews and G. Davidson, *J. Organomet. Chem.*, 1972, **36**, 340.

31 K. Hoffman and E. Weiss, *J. Organomet. Chem.*, 1982, **234**, C23.

32 M. Poliakoff and J. J. Turner, *J. Chem. Soc., Dalton Trans.*, 1973, 1351.

33 M. Poliakoff, *J. Chem. Soc., Dalton Trans.*, 1974, 210.

34 M. Kokkes, D. J. Stufkens, and A. Oskam, *J. Chem. Soc., Chem. Commun.*, 1983, 369.

35 W. Hubel and E. H. Braye, *J. Inorg. Nucl. Chem.*, 1959, **10**, 250.

36 M. King, E. M. Holt, P. Radnia, and J. S. McKennis, *Organometallics*, 1982, **1**, 1718.

37 B. F. G. Johnson, K. D. Karlin, and J. Lewis, *J. Organomet. Chem.*, 1978, **145**, C23.

38 P. S. Braterman, 'Metal Carbonyl Spectra,' Academic Press, London, 1975.

39 D. J. Taylor, Ph.D. Thesis, University of Southampton, 1981.

40 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 5th edn., Wiley Interscience, New York, 1988, ch. 24.

41 K. A. Mahmoud, A. J. Rest, and H. G. Alt, *J. Chem. Soc., Dalton Trans.*, 1985, 1365.

42 R. H. Hooker and A. J. Rest, *J. Organomet. Chem.*, 1982, **234**, C23.

43 D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, 1969, **51**, 278.

44 K. A. Mahmoud, A. J. Rest, and H. G. Alt, *J. Organomet. Chem.*, 1983, **246**, C37; *J. Chem. Soc., Dalton Trans.*, 1984, 187.

45 B. D. Moore, M. B. Simpson, M. Poliakoff, and J. J. Turner, *J. Chem. Soc., Chem. Commun.*, 1984, 972.

46 A. K. Campen, R. Narayanaswamy, and A. J. Rest, *J. Chem. Soc., Dalton Trans.*, 1990, 823.

47 K. Sonogushira and N. Hagihara, *Bull. Chem. Soc. Jpn.*, 1966, **39**, 1178.

48 E. H. Braye, W. Hubel, and I. Caplier, *J. Am. Chem. Soc.*, 1961, **83**, 4406.

49 A. A. Hock and O. S. Mills, *Acta Crystallogr., Sect. B*, 1961, **14**, 139.

50 E. O. Fischer, K. Bittles, and H. P. Fritz, *Z. Naturforsch.*, 1962, **186**, 83; R. P. Slidge, O. S. Mills, and V. Shomaker, *Proc. Chem. Soc.*, 1963, 380.

51 M. D. Rausch, B. H. Edwards, J. L. Atwood, and R. D. Rogers, *Organometallics*, 1982, **1**, 1567.

52 J. P. Collman, J. W. Kang, W. F. Little, and M. F. Sullivan, *Inorg. Chem.*, 1968, **7**, 1298.

53 D. L. Thorn and R. Hoffmann, *Nouv. J. Chim.*, 1979, **3**, 39.

54 M. R. Churchill and R. Mason, *Adv. Organomet. Chem.*, 1967, **5**, 120.

55 B. E. Bursten and R. F. Fenske, *Inorg. Chem.*, 1979, **18**, 1760.

56 A. J. Kos and P. von Rague Schleyer, *J. Am. Chem. Soc.*, 1980, **102**, 7928.

57 H. E. Zimmerman, *Acc. Chem. Res.*, 1971, **4**, 272.

58 W. J. R. Tyerman, M. Kato, P. Kebark, S. Masamune, O. P. Strauss, and H. E. Gunning, *Chem. Commun.*, 1967, 497.

Received 16*th January* 1990; *Paper* 0/00218F