Photochemistry of Tricarbonyl(η^4-cyclo-octatetraene)iron in a Methane Matrix at 12 K. Infrared Spectroscopic Evidence for Photoisomerisation and Carbon Monoxide Ejection Reactions †

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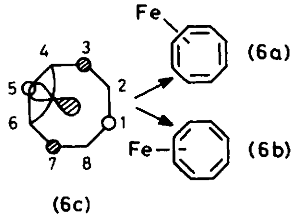
Fourier-transform infrared spectroscopic evidence, including ^{13}CO labelling and energy-factored CO force-field fitting, is presented to show that photolysis of [Fe('*tub*'-η^4-C_8H_8)(CO)$_3$] in a CH_4 matrix at 12 K leads to the formation of a [Fe('*chair*'-η^4-C_8H_8)(CO)$_3$] species *via* the [Fe(η^2-C_8H_8)(CO)$_3$] intermediate. An additional photoproduct is the co-ordinatively unsaturated species [Fe(η^4-C_8H_8)(CO)$_2$] formed by photoelimination of a CO ligand. The results are related to the fluxional behaviour of [Fe(η^4-C_8H_8)(CO)$_3$] in solution.

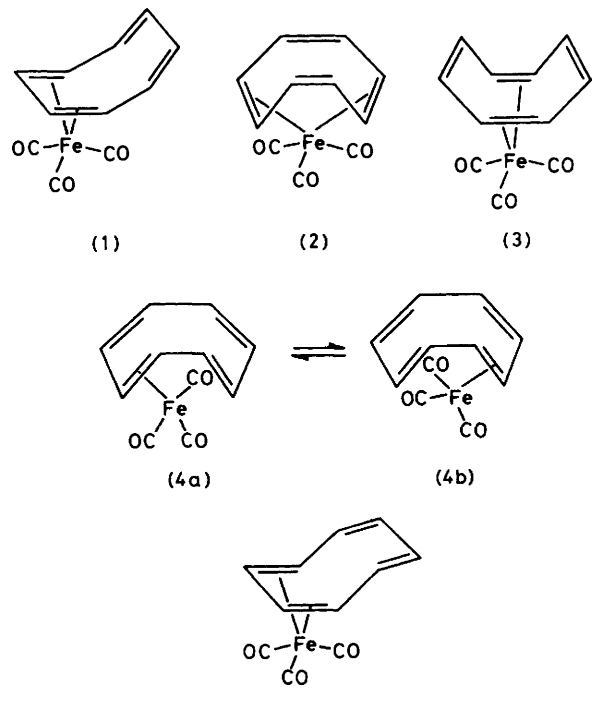
A single-crystal *X*-ray diffraction study of tricarbonyl(cyclo-octatetraene)iron showed that the [Fe(CO)$_3$] fragment, which has C_s symmetry, is bonded to a 1,3-diene fragment of the cyclo-octatetraene (cot) molecule.[1] There are a number of ways the cot molecule could bind [2-4] (Scheme 1) but the *X*-ray study [1] and a variety of spectroscopic studies, *e.g.* infrared and Raman,[5] low-temperature ^{1}H n.m.r.,[6,7] and Mössbauer,[8] all favour structure (1). This structure is henceforth denoted as [Fe('*tub*'-η^4-C_8H_8)(CO)$_3$] or [Fe('*tub*'-η^4-cot)(CO)$_3$].

The fluxional behaviour of [Fe(η^4-cot)(CO)$_3$] in solution and the solid state has been known for many years.[9] N.m.r. studies (^{1}H and ^{13}C) [6,10] are consistent with a rapid interconversion of isomers (6a) $\rightleftharpoons$ (6b) through 1,2-shifts of the ring carbon atoms. Interestingly, ^{13}C n.m.r. studies [10] of the CO ligands show that there is a rotation of the CO groups within the [Fe(CO)$_3$] unit, but that this is an independent process which occurs in addition to that involving the ring carbons. A perturbation molecular orbital approach has been used [11] to account for the fluxionality. It turns out that the two equivalent configurations for [Fe(η^4-cot)(CO)$_3$] (6a and 6b) are related by a 1,2-shift of the metal through a transition state such as (6c). It has been pointed out [11] that (6c) is a low activation energy intermediate since, in addition to the retention of interaction of the *dp* hybrid with the p_π orbital of C^5, it gains stabilisation from the positive overlap with the terminal carbon bonds during the 1,2-shift.



(6c)

Matrix isolation studies of a variety of organometallic complexes have led to the generation and characterisation of species which have been proposed as reaction intermediates.[12] Most of the studies have concentrated on metal carbonyls and substituted carbonyls, but recently unstable species have been reported which show changes in the mode of co-ordination of cyclic or open-chain polyenes to metals. For example, photolysis of [Co(η^5-C_5H_5)(CO)$_2$] in a CO matrix at 12 K led to the addition of a CO ligand and the (probable) change of ring co-ordination from η^5 to η^3; this process was reversible and as such is consistent with the associative mechanism proposed for ligand substitution reactions of [Co(η^5-C_5H_5)(CO)$_2$].[13] Photoinduced hydrogen migration has been found to occur at 12 K for [Re(η^5-C_5H_5)(η^2-C_5H_6)(CO)$_2$],[14] and thermal rearrangement has been found for [Mo(η^6-C_7H_8)(CO)$_3$],[15] to give [Re(η^5-C_5H_5)(σ-C_5H_5)(CO)$_2$(H)] and [Mo(η^5-C_7H_7)-(CO)$_3$(H)], respectively. The latter species is interesting because the well known thermal 1,5-hydrogen shift for [Mo(η^6-C_7H_8)(CO)$_3$] has been proposed [16,17] to proceed *via* a hydride species which could undergo internal rearrangement as a hydride with subsequent migration of the hydride back to the ring. In matrix isolation studies of [Fe(η^4-diene)(CO)$_3$] complexes the major process was found to be photoelimination of CO both for the cyclic diene complex [Fe(η^4-C_4H_4)-(CO)$_3$] [18] and for open chain diene complexes *e.g.* [Fe(η^4-C_4H_6)(CO)$_3$].[19] In the case of the latter, photodecomplexation of one end of the diene occurred [19] to give [Fe(η^2-C_4H_6)(CO)$_3$].



Scheme 1. Possible structural configurations of [Fe(η^4-cot)(CO)$_3$]

In this paper we report Fourier-transform infrared matrix isolation studies of the primary photochemical reactions of

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† *Non-S.I. unit employed:* 1 Torr = (101 325/760) Pa.

$[\mathrm{Fe}(\eta^4\text{-cot})(\mathrm{CO})_3]$ in CH_4 matrices at 12 K, and relate the results to studies of the fluxionality of the complex.

Experimental

Cryogenic temperatures (*ca.* 12 K) were obtained by using a Displex CSA-202 closed-cycle helium refrigeration system (Air Products and Chemicals Inc.). The complex $[\mathrm{Fe}(\eta^4\text{-cot})(\mathrm{CO})_3]$ was not volatile enough to give a gas mixture for ' pulsed ' or direct slow ' spray-on ' deposition. However, modest heating (20—24 °C) of a sample held in a sublimation finger provided vapour which was co-condensed with a large excess of CH_4 on to the cold CsI window. Deposition (*ca.* 2 h) was monitored throughout by scanning i.r. spectra of the matrix and checking that the half-width at half-height of the terminal CO-stretching bands did not exceed *ca.* 2 cm^{-1}, and that there was no tailing of the bands to lower wavenumbers. These monitoring tests, together with a substantially higher matrix gas flow than flow of vapour from the solid $[\mathrm{Fe}(\eta^4\text{-cot})(\mathrm{CO})_3]$, were designed to produce monomer isolation, *i.e.* single $[\mathrm{Fe}(\eta^4\text{-cot})(\mathrm{CO})_3]$ molecules completely surrounded by CH_4 molecules such that there would be a very low probability of any $[\mathrm{Fe}(\eta^4\text{-cot})(\mathrm{CO})_3]$ having another $[\mathrm{Fe}(\eta^4\text{-cot})(\mathrm{CO})_3]$ molecule as a nearest neighbour.

Infrared spectra were recorded with a Nicolet 7199 FT-IR spectrometer. ' Spectral stripping ' [20] was accomplished by subtracting the spectrum of the parent compound after deposition from the spectrum obtained after a period of photolysis. In such subtractions the subtraction factor was adjusted iteratively just to remove the bands due to the parent compound. U.v.–visible spectra were recorded with a Pye-Unicam SP 1800B spectrometer.

The radiation source was a water-cooled medium-pressure mercury arc lamp (Philips HPK 125-W). Wavelength-selective irradiation was achieved by using the following combinations of absorbing materials: filter A, $290 < \lambda < 370$ nm, quartz gas cell (pathlength 25 mm) containing Br_2 gas (300 Torr) + Pyrex glass disc (4 mm thick); filter B, $\lambda > 410$ nm, Corning Glass Color filter CS3-74 (4 mm thick).

The matrix gas (CH_4) was B.O.C. ' Grade X ' purity and ^{13}CO (95% enriched) was obtained from B.O.C. Prochem Limited. The sample of $[\mathrm{Fe}(\eta^4\text{-cot})(\mathrm{CO})_3]$ [21] was a gift from Dr. N. Connelly and was purified by sublimation prior to use in matrix isolation experiments. The ^{13}CO-enriched complex $[\mathrm{Fe}(\eta^4\text{-cot})(\mathrm{CO})_3]$ was prepared by irradiating (filter A) a sample in hexane (25 mg in 100 cm^3) in an atmosphere of ^{13}CO (300 Torr) for 4 h. Such a period of irradiation was sufficient to produce a mixture of mono-, di-, and tri-^{13}CO-enriched complexes as indicated by subsequent i.r. spectra. The solvent was removed by pumping under vacuum and the red solid was purified by sublimation (20—30 °C; 0.5 Torr).

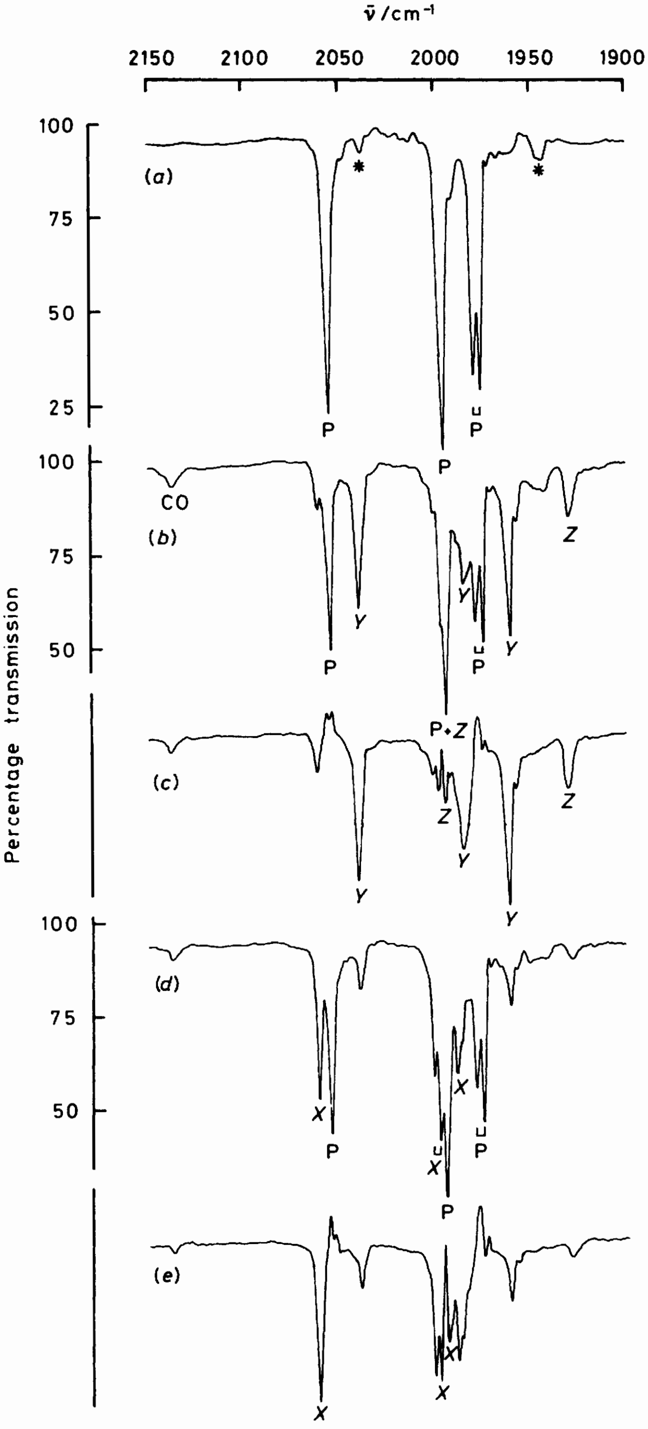


Figure. Infrared spectra from an experiment with $[\mathrm{Fe}(\eta^4\text{-cot})(\mathrm{CO})_3]$ (bands marked P) isolated at high dilution in a CH_4 matrix at 12 K: (*a*) after deposition, (*b*) after 30 min irradiation using filter A, (*c*) difference spectrum [(*b*) − A(*a*)], (*d*) after further 30 min photolysis using filter B, and (*e*) difference spectrum [(*d*) − A′(*a*)], where A and A′ are scaling constants. Bands marked with an asterisk are due to $[\mathrm{Fe}(\eta^4\text{-cot})(^{12}\mathrm{CO})_2(^{13}\mathrm{CO})]$ in natural abundance. Product bands are marked *X*, *Y*, and *Z* and are identified with species (5), (7), and (8), respectively

Results

Photolysis of $[\mathrm{Fe}(\eta^4\text{-cot})(\mathrm{CO})_3]$ *in a* CH_4 *Matrix at* 12 *K.*— On deposition the i.r. spectrum of $[\mathrm{Fe}(\eta^4\text{-cot})(\mathrm{CO})_3]$ isolated at high dilution in a CH_4 matrix showed the characteristic pattern in the terminal CO-stretching region for a C_s $[\mathrm{Fe}(\mathrm{CO})_3]$ fragment having three strong absorption bands at 2054.1 (*A′*), 1994.1 (*A′*) and 1976.2 cm^{-1} (matrix split band, *A″*) [Figure (*a*)]. The electronic absorption spectrum of $[\mathrm{Fe}(\eta^4\text{-cot})(\mathrm{CO})_3]$ in a CH_4 matrix at 12 K showed a strong absorption ($\lambda_{max.}$ 300 nm) and a weak absorption ($\lambda_{max.}$ 410 nm). The weak absorption tailed into the visible region.

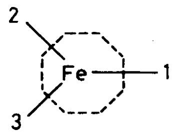
A period of u.v. irradiation ($290 < \lambda < 370$ nm; filter A) produced new bands at 2138.4 (' free ' CO), 2059.7, 2038.6, 1983.3, 1960.3, and 1929.6 cm^{-1} with weak shoulders on the

Table 1. Observed and calculated[a] band positions (cm^{-1}) of terminal CO-stretching bands for ^{13}CO-enriched [Fe(η^4-cot)(CO)$_3$] and its photolysis products in a CH$_4$ matrix at 12 K

Complex	Point group	ν_{CO}	Obs.		Calc.
(1) [Fe('*tub*'-η^4-cot)(^{12}CO)$_3$]	C_s	A'	2 054.1		2 053.7
		A'	1 994.1		1 993.7
		A''	1 977.9 1 974.4 [b]	1 976.2	1 975.6
[Fe('*tub*'-η^4-cot)(^{12}CO)$_2$(^{13}CO)]	C_s [c]	A'	2 039.2 2 036.3 [b]	2 037.8	2 038.4
		A''	1 977.9 1 974.4 [b]	1 976.2	1 975.6
		A'	1 963.4		1 964.0
	C_1 [d]	A	2 046.2		2 046.2
		A	1 988.9		1 989.2
		A	1 942.4		1 943.2
[Fe('*tub*'-η^4-cot)(^{12}CO)(^{13}CO)$_2$]	C_1 [e]	A	2 026.7 2 024.9 [b]	2 025.8	2 026.4
		A	[f]		1 966.6
		A	1 939.9		1 940.7
	C_s [g]	A'	2 039.2 2 036.3 [b]	2 037.8	2 038.4
		A'	1 963.4		1 964.0
		A''	1 932.8 1 929.6 [b]	1 931.2	1 931.7
[Fe('*tub*'-η^4-cot)(^{13}CO)$_3$]	C_s	A'	2 007.6		2 008.2
		A'	1 948.9		1 949.4
		A''	1 932.8 1 929.6 [b]	1 931.2	1 931.7
(5) [Fe('*chair*'-η^4-cot)(^{12}CO)$_3$]	C_s	A'	2 059.7		2 059.8
		A'	2 000.6 1 997.3 [b]	1 999.0	1 999.9
		A''	1 987.7		1 987.8
[Fe('*chair*'-η^4-cot)(^{12}CO)$_2$(^{13}CO)]	C_s [c]	A'	[f]		2 042.8
		A''	1 987.7		1 987.8
		A'	[f]		1 971.9
	C_1 [d]	A	2 054.1		2 053.3
		A	1 997.3		1 996.3
		A	[f]		1 953.3
[Fe('*chair*'-η^4-cot)(^{12}CO)(^{13}CO)$_2$]	C_1 [e]	A	2 032.5		2 031.6
		A	1 977.2		1 976.1
		A	1 950.7		1 950.0
	C_s [g]	A'	2 046.9		2 046.3
		A'	[f]		1 968.3
		A''	1 943.7		1 943.6
[Fe('*chair*'-η^4-cot)(^{13}CO)$_3$]	C_s	A'	2 014.1		2 014.1
		A'	[f]		1 955.4
		A''	1 943.7		1 943.6
(7) [Fe(η^2-cot)(^{12}CO)$_3$]	C_s	A'	2 038.6		2 039.1
		A'	1 983.3		1 983.7
		A''	1 960.3		1 959.7
[Fe(η^2-cot)(^{12}CO)$_2$(^{13}CO)]	C_s [c]	A'	[f]		2 023.5
		A''	1 960.3		1 959.7
		A'	[f]		1 954.5
	C_1 [d]	A	2 032.8		2 032.1
		A	1 978.4		1 977.9
		A	[f]		1 928.3

Table 1 (*continued*)

Complex	Point group	ν_{CO}	Obs.	Calc.
[Fe(η^2-cot)(^{12}CO)(^{13}CO)$_2$]	C_1 [e]	A	2 012.0	2 011.4
		A	1 956.1	1 955.5
		A	[f]	1 926.7
	C_s [g]	A'	2 025.5	2 025.2
		A'	1 952.5	1 952.8
		A''	1 915.5	1 916.1
[Fe(η^2-cot)(^{13}CO)$_3$]	C_s	A'	1 994.1	1 993.8
		A'	1 939.9	1 939.6
		A''	1 915.5	1 916.1
(8) [Fe(η^4-cot)(^{12}CO)$_2$]	C_{2v} [h]	A_1	1 994.1	1 993.6
		B_1	1 929.6	1 928.8
[Fe(η^4-cot)(^{12}CO)(^{13}CO)]	C_s	A'	1 978.4	1 978.2
		A''	1 898.7	1 900.6
[Fe(η^4-cot)(^{13}CO)$_2$]	C_{2v} [h]	A_1	1 948.9	1 949.3
		B_1	1 885.1	1 885.9



(A)

Complex	K_1	K_2	k_{12}	k_{23}
(1)	1 654.9	1 615.9	34.7	39.0
(5)	1 699.9	1 628.2	34.6	31.9
(7)	1 637.0	1 592.0	31.8	40.5
	K	k_i		
(8)	1 554.3	51.4		

[a] Refined energy-factored force constants (N m^{-1}) as defined by the numbering in (A), *i.e.* $1 \neq 2 = 3$. [b] Matrix splitting: mean band position used for iterative computer force field fitting. [c] ^{13}CO in position 1. [d] ^{13}CO in position 2. [e] ^{12}CO in position 2. [f] Band obscured by overlap. [g] ^{12}CO in position 1. [h] Local symmetry of Fe(CO)$_2$ fragment.

higher frequency side of the 1994.1 cm^{-1} parent band [Figure (*b*)]. Further irradiation caused the intensities of the ' free ' CO band and the bands at 2038.6, 1983.3, 1960.3, and 1929.6 cm^{-1} to increase substantially with corresponding decrease of the parent bands. The intensity of the band at 2059.7 cm^{-1} remained constant. Careful differential band pattern subtraction [Figure (*c*)] revealed that the parent band at 1994.1 cm^{-1} decreased in intensity less than the parent molecule band at 2054.1 cm^{-1}, *i.e.* a new band was growing which was overlapping the 1994.1 cm^{-1} band.

After 30 min irradiation with visible light ($\lambda > 410$ nm; filter B) the band of ' free ' CO, and those at 2038.6, 1983.3, 1960.3, and 1929.6 cm^{-1} decreased, and the band at 2059.7 cm^{-1} increased; concomitantly further new bands at 2000.6, 1997.3, and 1987.7 cm^{-1} appeared [Figure (*d*)]. The latter bands correspond to shoulder bands in the previous photolysis stage. The subtraction spectrum [Figure (*e*)] shows more clearly the new bands produced from the photoreaction of [Fe(η^4-cot)(CO)$_3$]. Annealing the matrix to 35 K caused the ' free ' CO band and the bands at 1929.6 cm^{-1} to decrease and the parent bands to increase.

In a separate experiment, where the sequence of irradiation steps was reversed, *i.e.* upon visible irradiation (filter B) of [Fe(η^4-cot)(CO)$_3$] after deposition, an i.r. spectrum similar to that in Figure (*d*) was produced, but without the formation of bands due to ' free ' CO and the band at 1929.6 cm^{-1}. On further irradiation with u.v. light (filter A) a spectrum similar to that in Figure (*b*) was obtained.

The new bands that appear in the matrix photoreactions of [Fe(η^4-cot)(CO)$_3$] can be grouped into three sets: bands marked *X* (2059.7, 2000.6, 1997.3, and 1987.7 cm^{-1}); bands marked *Y* (2038.6, 1983.3, and 1960.3 cm^{-1}); and bands marked *Z* [2138.4 (' free ' CO), 1994.1 and 1929.6 cm^{-1}] (see Figure). In order to establish unequivocally the number of CO ligands in the products corresponding to *X*, *Y*, and *Z*, a study of the ^{13}CO-enriched molecule was made.

Photolysis of [Fe(η^4-cot)(^{12}CO)$_n$(^{13}CO)$_{3-n}$] *in a* CH$_4$ *Matrix at* 12 *K*.—Irradiation of [Fe(η^4-cot)(^{12}CO)$_n$(^{13}CO)$_{3-n}$] in a CH$_4$ matrix at 12 K using the sequence of irradiation and annealing found appropriate for [Fe(η^4-cot)(CO)$_3$] gave band patterns for the ^{13}CO-enriched molecules corresponding to the species with band sets *X*, *Y*, and *Z*. These mixed ^{12}CO/^{13}CO band patterns were subjected to an energy-factored force-field fitting procedure [22,23] in order to ascertain the number of carbonyl ligands in each case. The excellent agreement (Table 1) of the observed and calculated bands, not only for the parent compound (1) but also for the products, confirms that band sets *X* and *Y* originate from [Fe(CO)$_3$] fragments while band set *Z* corresponds to a [Fe(CO)$_2$] unit.

Table 2. Infrared band positions (cm^{-1}) in the terminal metal carbonyl stretching region for [Fe(η^4-cot)(CO)$_3$] and [Fe(η^4-butadiene)(CO)$_3$] and their photolysis products in gas matrices at 12 K

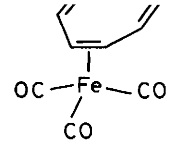
	Polyolefin (L)	
Complex	Cyclo-octatetraene [a]	Buta-1,3-diene [b,c]
[Fe(η^4-L)(CO)$_3$]	2 054.1	2 060
	1 994.1	1 995
	1 976.2	1 983
[Fe(η^2-L)(CO)$_3$]	2 038.6 [d]	2 029
	1 983.3	1 970
	1 960.3	1 953
[Fe(η^4-L)(CO)$_2$]	1 994.1 [e]	2 009
	1 929.6	1 944

[a] CH_4 matrix. [b] Ar matrix. [c] Data from ref. 19. [d] Species (7). [e] Species (8).

Discussion

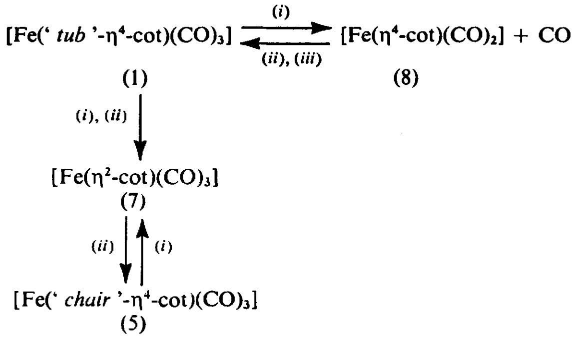
Structural Assignments for the New Species.—Energy-factored force-field fitting has established (Table 1) that the species characterised by band set *X* contains a [Fe(CO)$_3$] fragment. The closeness of the set *X* band positions (2059.7, 1999.0, and 1987.7 cm^{-1}) to those of the parent molecule (1) (2054.1, 1994.1, and 1976.2 cm^{-1}) suggests that no great change in the electron density at the metal has occurred, although the small shift to higher wavenumbers as compared with (1) must have some significance, *e.g.* a change in the mode of ring co-ordination. The fact that the set *X* bands are at higher wavenumbers than for (1) immediately rules out any species with dechelation of part of the cot ligand, *i.e.* [Fe(η^2-cot)(CO)$_3$], because such a step in the case of [Fe(η^4-C_4H_6)(CO)$_3$] (ν_{CO} at 2 060, 1 995, and 1 983 cm^{-1}) led to an appreciable shift to lower wavenumbers when [Fe(η^2-C_4H_6)(CO)$_3$] (ν_{CO} at 2 029, 1 970, and 1 953 cm^{-1}) was produced.[19] An even greater shift was observed when a CO ligand was ejected, *e.g.* [Fe(η^4-C_4H_6)(CO)$_2$] (ν_{CO} at 2 009 and 1 944 cm^{-1}).[19] One of the possible contenders [(2)—(5); Scheme 1], structure (4), can be eliminated because the instantaneous structure has an η^2-cot ligand, and additionally two conformations would be expected to be frozen out at 12 K, *cf.* the two conformations of the acetyl ligand frozen out at 12 K for [Fe(η^5-C_5H_5)(CO)$_2$(COCH$_3$)] and for [Mn(CO)$_5$(COCH$_3$)].[24,25] The formation of two of the other possible contenders, (2) and (3), would require considerable changes in the conformation of the cot ligand together with a shift of the [Fe(CO)$_3$] fragment with respect to the ring. Both processes would require a large input of energy and additionally there would have to be a relaxation of the host matrix cage of molecules packing in and around each substrate molecule. It seems unlikely that absorption of photons in the region $\lambda > 410$ nm (<290 kJ mol^{-1}) could provide the energy needed to produce (2) and (3). The remaining possibility (5) is the structure adopted by the osmium analogue, [Os(η^4-cot)(CO)$_3$].[26] Formation of (5) requires no movement of the [Fe(CO)$_3$] fragment but only the flipping of the ring. It seems likely that set *X* bands can be assigned to (5), *i.e.* [Fe(' *chair* '-η^4-cot)(CO)$_3$].

Energy-factored force-field fitting has also established (Table 1) that the species characterised by band set *Y* contains a [Fe(CO)$_3$] fragment. In deciding among the various structures two factors need to be taken into consideration: the radiation energy and the terminal CO-stretching band positions. The high energy radiation source used ($290 < \lambda < 370$ nm) could probably provide sufficient energy to produce the necessary conformation changes in the formation of (2) and (3) (Scheme 1) if there could be relaxation of the matrix cage. Species (2) and (3), however, still contain two olefin and three carbonyl ligands bound to the iron and, therefore, would be expected to exhibit terminal CO-stretching bands much closer to those of [Fe(' *tub* '-η^4-cot)(CO)$_3$] than actually observed in band set *Y*, *cf.* closeness of bands of [Fe(' *chair* '-η^4-cot)(CO)$_3$] and even [Fe(η^4-C_4H_6)(CO)$_3$] (Table 2). The fact that the set *Y* bands are significantly shifted to lower wavenumbers in comparison with (1) suggests that dechelation of part of the cot ligand has occurred. Although the downward shift for the process [Fe(η^4-C_4H_6)(CO)$_3$] $\longrightarrow$ [Fe(η^2-C_4H_6)(CO)$_3$] is approximately twice that observed for [Fe(η^4-cot)(CO)$_3$] and its photoproduct, it is worth remembering that there is one adjacent olefin when butadiene binds as an η^2-ligand and also that the diene probably adopts an s-*trans*-conformation (see later). If the cot ligand were to bind as an η^2-ligand there would be two adjacent olefins with overall s-*cis*-conformations. Such η^2-binding for cot was observed when (1) was converted into [Fe(η^2-cot)(CO)$_4$] and ultimately [Fe(CO)$_5$] in a CO matrix.[27] On balance it seems more likely that the species responsible for the set *Y* bands is [Fe(η^2-cot)(CO)$_3$]. Structure (7) was chosen rather than (4) because the former would require a minimum conformational change in the ring during generation from (1). This factor is of considerable importance in view of the fact that the species (7) must be capable of interconversion between (1) and (5). It is interesting that, whereas photolysis of [Fe(η^2-C_4H_6)(CO)$_4$] in an Ar matrix at 12 K gave [Fe(η^2-C_4H_6)(CO)$_3$] and [Fe(η^4-C_4H_6)(CO)$_3$], only [Fe(η^4-cyclohexa-1,3-diene)(CO)$_3$] was observed to be formed on photolysis of [Fe(η^2-cyclohexa-1,3-diene)(CO)$_4$].[19] This result was ascribed [19] to the ability of the open chain diene complex [Fe(η^2-C_4H_6)(CO)$_3$] intermediate to undergo s-*cis* $\longrightarrow$ s-*trans* interconversion, which is a photoreaction rather than a thermal process, whereas the parent cyclic diene complex [Fe(η^2-cyclohexadiene)(CO)$_4$] is locked in an s-*cis*-configuration. In such a situation the co-ordinatively unsaturated species [Fe(η^2-cyclohexadiene)(CO)$_3$] would not be able to rearrange, and hence goes on to give [Fe(η^4-cyclohexadiene)(CO)$_3$]. The observation of the η^2-cyclic diene complex [Fe(η^2-cot)(CO)$_3$] probably arises because the cot ligand has at least two s-*cis* butadiene units, and it is the ability to switch between a number of pairs of units which allows a rearrangement process analogous to the s-*cis* $\longrightarrow$ s-*trans* rearrangement for [Fe(η^2-C_4H_6)(CO)$_3$].



(7)

Similarly the species associated with band set *Z* formed together with ' free ' CO has been shown by ^{13}CO labelling to contain a [Fe(CO)$_2$] fragment and, on the basis of a comparison with [Fe(η^4-C_4H_6)(CO)$_2$] (Table 2), is identified as [Fe(η^4-cot)(CO)$_2$] (8). The reactivity of (8) is demonstrated by its recombination with CO on annealing the matrix, *i.e.* raising the temperature to *ca.* 35 K for a short period (2 min) and then re-cooling to 12 K, or irradiation with visible light.



Scheme 2. (*i*), *h*ν (filter A); (*ii*), *h*ν (filter B); (*iii*), anneal

Reactions and Equilibria.—The photoreactions of (1) in a CH_4 matrix are summarised in Scheme 2. The various equilibria indicate that species (7) could probably be the intermediate for the $(1) \rightleftarrows (5)$ interconversion. The dechelation of one double bond to give [Fe(η^2-cot)(CO)$_3$] could allow a change in the conformation of the cot ligand from '*tub*' to '*chair*' and *vice versa*. The photoreactions observed are similar to those of [Fe(η^4-1,3-C_4H_6)(CO)$_3$] rather than to those of [Fe(η^4-cyclohexadiene)(CO)$_3$], where no η^2-species was detected.[19]

Unravelling the complex band patterns for these equilibria would have been impossible without the aid of a Fourier-transform infrared spectrometer. This work is one of the first such isolation studies of an organometallic complex to employ such a spectrometer. In further work we will endeavour (*a*) to probe details of the metal–ring co-ordination *via* ν(C=C) and ν(metal–ring) vibrations, (*b*) to seek information concerning which CO ligand in (1) is substituted *via* the use of reactive matrices (N_2, C_2H_4), and (*c*) to investigate other sizes and potential hapticities of rings bound to iron, *e.g.* [Fe(η^4-cyclo-octadiene)(CO)$_3$] and [Fe(η^4-cycloheptatriene)(CO)$_3$].

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