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The Solution Dynamics of Some $Fe_2(CO)_6(L-L')$ Complexes

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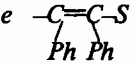
The variable temperature solution dynamics of some compounds of the $Fe_2(CO)_6(L-L')$ class, where L–L' is $-C(Ph)=C(Ph)-S-$ (I) or $-C_6H_4-CH_2-N(R)-$ (II), were observed by ^{13}C NMR spectra. The single-crystal X-ray structure determination of $Fe_2(CO)_5PPh_3[-C(Ph)=C(Ph)-S-]$ demonstrated that the triphenylphosphine group was attached to the original "π-$Fe(CO)_3$" group. This aided in the assignment of the carbonyl carbon resonances of I at low temperature. At room temperature the

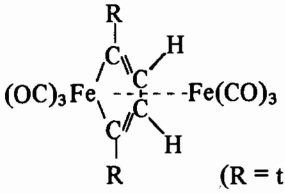


$-\underset{Ph}{C}=\underset{Ph}{C}-S$

ligand is rapidly undergoing a fluxional process which makes the two $Fe(CO)_3$ groups equivalent. Similar fluxional motions appear to be occurring for type-II compounds also.

Introduction

Recently we have reported on the solution dynamics of some tricarbonylferrole–iron tricarbonyl derivatives [1]. For most molecules of this type the π-$Fe(CO)_3$ group is fluxional over the temperature range +90 °C to –120 °C. One exception is the derivative



(R = t-Bu)

for which both $Fe(CO)_3$ groups were found to be static at low temperature (–100 °C) [2]. For these compounds there was no evidence for carbonyl exchange between iron atoms nor for diene ligand movement which would interchange the bonding roles of the two $Fe(CO)_3$ units.

The tricarbonylferrole–iron tricarbonyl compounds are a small portion of a much larger class of compounds of the general formula $Fe_2(CO)_6(L-L')$. Considerable NMR data are available on a class of compounds where the L–L' unit is a large cyclic polyene [3–5]. Again, in these cases the variable temperature ^{13}C NMR spectra of the CO groups provide information about the movement of the $Fe_2(CO)_6$ group relative to the L–L' unit. In these fluxional processes it is believed that there is a local interchange of carbonyl groups on a given $Fe(CO)_3$ group but no exchange of carbonyl groups occurs between different $Fe(CO)_3$ groups.

We report here a solution NMR study of selected compounds of the $Fe_2(CO)_6(L-L')$ type, in which the L–L' unit is a more open, chain-like structure (as illustrated in Fig. 1).

Experimental

Instrumentation and ^{13}C NMR Procedures

The ^{13}C NMR spectra were obtained with a Varian XL-100-15 spectrometer operating in the pulsed Fourier transform mode at 25.2 MHz, ^1H NMR spectra were recorded at 100 MHz on the same instrument. The instrument is equipped with a Transform Technology, Inc. pulse unit which delivers a 90° pulse in 20 μsec and a 36 K Nicholet 1089 computer system with disk. Carbon-13 NMR spectra (67.9 MHz) were obtained with a Brüker HX-270 spectrometer with a 10 mm probe operating in the pulsed Fourier transform mode. The instrument is equipped with a Transform Technology, Inc. pulse unit which delivers a 90° pulse in 15 μsec and a 20K Nocholet 1080 computer system with disk. The ^{13}C chemical shifts were measured relative to an internal solvent peak and reported relative to tetramethylsilane. The conversion factor used was $\delta(TMS)=\delta(CH_2Cl_2) + 53.89$ ppm. To reduce T_1 relaxation times tris(acetylacetonato)chromium(III) (about 0.05 *M*) was added to each NMR sample [6].

Materials

The compounds $Fe_2(CO)_6(-S-C(Ph)=C(Ph)-)$ [7], $Fe_2(CO)_5PPh_3[-S-C(Ph)=C(PH)-]$ [7], and $Fe_2(CO)_6(C_6H_4CH_2NR)$ where R=Ph or CH_3 [8] were prepared from literature methods.

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*Contribution No. 3080.

TABLE I. Final Positional and Thermal Parameters for $Fe_2(CO)_5PPh_3$(–S–C(Ph)=C(Ph)–).

Atom	10^5x	10^5y	10^5z	10^5b_{11} or B_{iso}	10^5b_{22}	10^5b_{33}	10^5b_{12}	10^5b_{13}	10^5b_{13}
Fe(1)	11189(3)	7260(6)	36731(8)	60(1)	166(4)	310(8)	6(2)	14(3)	3(5)
Fe(2)	6196(4)	15950(6)	47379(9)	63(1)	157(4)	421(9)	6(2)	24(3)	-0(5)
P(1)	10708(7)	-2755(11)	26196(17)	76(3)	202(7)	423(16)	19(4)	-19(5)	-32(9)
S(1)	5590(6)	3330(10)	47776(16)	46(2)	151(6)	336(15)	-4(3)	5(5)	-7(8)
O(1)	8376(23)	17317(33)	19359(49)	219(12)	300(24)	463(50)	124(14)	48(20)	166(30)
O(2)	20746(20)	8971(34)	32528(48)	74(8)	437(28)	635(51)	-5(12)	42(17)	35(31)
O(3)	3288(19)	18584(32)	69993(51)	118(9)	304(24)	524(52)	-12(11)	69(17)	-88(29)
O(4)	-2053(20)	19368(33)	34576(52)	87(8)	313(24)	888(61)	24(12)	-72(19)	103(32)
O(5)	10116(19)	30599(32)	43159(49)	102(8)	203(21)	746(54)	-2(11)	43(17)	87(28)
C(1)	11052(24)	4074(41)	53400(57)	64(10)	230(28)	228(53)	-25(14)	16(20)	-81(32)
C(2)	11999(24)	11624(36)	52464(60)	70(10)	87(24)	376(58)	1(12)	27(21)	-83(31)
C(3)	9294(27)	13494(44)	26555(73)	100(12)	186(28)	457(70)	25(15)	67(24)	-45(39)
C(4)	16935(30)	8302(44)	34074(61)	96(12)	262(32)	289(59)	19(16)	-13(22)	-15(35)
C(5)	4357(26)	17695(42)	61145(78)	74(11)	162(28)	626(80)	-4(14)	-10(24)	-83(39)
C(6)	1101(29)	17992(43)	39455(75)	71(11)	168(28)	727(80)	-8(15)	71(26)	-2(39)
C(7)	8475(25)	25011(53)	44875(62)	61(10)	256(31)	412(65)	71(17)	42(21)	25(39)
C(11)	13399(25)	-2126(41)	59046(62)	23(1)					
C(12)	10929(26)	-7826(44)	63579(67)	31(2)					
C(13)	13060(30)	-13512(50)	69354(76)	39(2)					
C(14)	17626(30)	-13221(49)	70749(74)	39(2)					
C(15)	20133(28)	-7687(47)	65958(69)	35(2)					
C(16)	18030(26)	-2174(43)	60042(65)	29(2)					
C(21)	15655(25)	15541(42)	58131(62)	24(1)					
C(22)	16200(27)	14534(46)	69312(67)	32(2)					
C(23)	19406(30)	18543(46)	75111(77)	39(2)					
C(24)	21918(30)	23783(52)	69885(77)	44(2)					
C(25)	21444(27)	25030(51)	58986(73)	36(2)					
C(26)	18298(26)	20905(42)	52889(65)	28(2)					
C(31)	11591(26)	88409(42)	33288(64)	27(2)					
C(32)	15835(28)	-12996(47)	37811(72)	35(2)					
C(33)	16600(29)	-19634(49)	43374(71)	37(2)					
C(34)	13194(30)	-24512(55)	44632(77)	43(2)					
C(35)	8977(30)	-23191(51)	40625(80)	42(2)					
C(36)	8233(27)	-16701(45)	34758(70)	34(2)					
C(41)	14664(25)	-2881(41)	14533(63)	25(1)					
C(42)	17689(28)	-8479(45)	12600(70)	34(2)					
C(43)	20513(31)	-8084(50)	3408(75)	42(2)					
C(44)	20221(31)	-2253(51)	-3639(74)	41(2)					
C(45)	17171(31)	3389(50)	-1847(77)	42(2)					
C(46)	14449(30)	3132(49)	7354(76)	39(2)					
C(51)	5301(24)	-4141(39)	19042(60)	22(1)					
C(52)	4925(26)	-9694(44)	11113(68)	31(2)					
C(53)	850(29)	89210(49)	5806(70)	37(2)					
C(54)	-2815(28)	-6300(47)	8298(69)	33(2)					
C(55)	-2415(28)	-1128(47)	16182(70)	34(2)					
C(56)	1590(27)	53(44)	21722(65)	30(2)					

Form of the exponential is: $\exp[-(h^2b_{11}+k^2b_{22}+l^2b_{33}+2hkb_{12}+2hlb_{13}+2klb_{23})]$

Crystallography

Crystals of $Fe_2(CO)_5PPh_3$(–S–C(Ph)=C(Ph)–) were recrystallized from methylene chloride-isooctane and occurred as various morphological forms. A small well-formed crystal of maximum dimension 0.25 mm bounded by the [100], [010] and [001] pinacoids was utilized for all data collection. Precision photographs and a systematic search of reciprocal space on the goniostat indicated uniquely the space group Pbca (#61, D_{2h}^{15}), and a least squares fit of angular settings for 14 reflections centered in $\pm 2\theta$ at -160 °C yielded cell parameters of a = 28.896(15), b = 18.127(10) and c = 12.169(9)Å. The calculated density for Z = 8 is 1.51 gm/cm^3. Data were collected at -160 °C using a gaseous nitrogen cold stream. The diffractometer used was a locally constructed computer controlled Picker goniostat system [9] equipped with a highly oriented graphite monochromator and molybdenum source (λ, MoK_α = 0.71069Å). A total of 5350 partially redundant data were collected using standard θ–2θ scan techniques, with a scan speed of 3.0°/min and 10 second background counts symmetrically disposed 0.75° on either side of the calculated position of the Kα_1 and Kα_2 doublet. Three orthogonal reflections chosen as standards were periodically monitored and indicated no systematic trends in the data. The raw data were reduced to 4289 unique intensities, of which 3290 (76.7%) were greater than their corresponding error based on counting statistics and were considered observed. An ignorance factor of 0.05 was used in the data reduction formula which is given elsewhere [10]. The data were corrected for absorption (μ, MoK = 10.64 cm^{-1}).

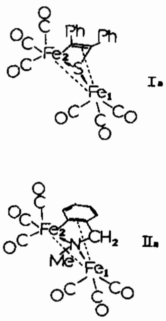
The position of the iron and sulfur atoms were determined by direct methods [11] and confirmed by Patterson techniques. All other non-hydrogen atoms were located by three successive Fourier synthesis, based on the known fragment. The structure was refined by full-matrix least squares, in which hydrogens were placed in calculated positions (d(C–H) = 0.95Å) and given fixed isotropic thermal parameters (B_{iso} = 3.5 Å^2), phenyl carbons were given isotropic thermal parameters, and all remaining atoms

TABLE II. ^{13}C Chemical Shifts for Some $Fe_2(CO)_6(L\text{–}L')$ Complexes.

Compound	Temp, °C	δ_c, ppm[a]				
		Fe(2) Carbonyls	Fe(1) Carbonyls	Ligand Ring		
				C(adjacent)[b]	C(remote)[c]	CH_2
$Fe_2(CO)_6(\text{–}S\text{–}C(Ph){=}C(Ph)\text{–})$ (Ia)	+30	209.2(6)		157.0	120.4	–
	–120	204.6(1) $209.6_3(1)$	209.6(4)	154.7	118.1	–
$Fe_2(CO)_5(PPh_3)(\text{–}S\text{–}C(Ph){=}C(Ph)\text{–})$ (Ib)	+30	209.4(3)	220.4 ($J_{P\text{–}C}$ = 16.6Hz) 219.4(1) ($J_{P\text{–}C}$ = 23.9Hz)	152.8	118.1	–
	–120	210.3(2) 204.5(1)	221.2(1) ($J_{P\text{–}C}$ = 17.0Hz) 220.0(1) ($J_{P\text{–}C}$ = 26.7Hz)	151.5	115.9	–
$Fe_2(CO)_6(C_6H_4CH_2NCH_3)$ (IIa)	+30	210.4(6)		146.3	124.1	75.3
	–120	211.9(2) 211.5(2) 209.7(2)		148.2	121.6	75.3
$Fe_2(CO)_6(C_6H_4CH_2NC_6H_5)$ (IIb)	+30	210.3(6)		149.04	122.70	75.2
	–120	211.0(2) 210.9(2) 209.4(2)		150.4	121.93	74.0

[a] Spectra measured in CH_2Cl_2. [b] Ring carbon adjacent to metal. [c] Ring carbon not adjacent to metal.

were given anisotropic thermal parameters. An isotropic extinction parameter was introduced when the refinement was nearly converged and was essentially zero, so subsequent cycles assumed no extinction. Final residuals were R(F) = 0.081 and $R_w(F)$ = 0.063, where $R(F) = \Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$ and $R_w(F) = \Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2$. The function minimized was $\Sigma w(|F_o|-|F_c|)$ where $w = 1/\sigma|F_o|$. The "goodness of fit" for the last cycle was 1.51 and the largest Δ/σ was 0.11. Final positional and thermal parameters are listed in Table I and structure amplitudes and other crystallographic data are also available [12].



I.

II.

Figure 1. Structures and numbering of the $Fe_2(CO)_6(L\text{–}L')$ complexes.

Results

$Fe_2(CO)_6(\text{–}S\text{–}C(Ph){=}C(Ph)\text{–})$ (Ia) and $Fe_2(CO)_5PPh_3(\text{–}S\text{–}C(Ph){=}C(Ph)\text{–})$ (Ib)

The ^{13}C NMR spectrum of Ia at room temperature at 25.2 MHz and 67.9 MHz contained one sharp singlet in the carbonyl carbon region (see Table II for shielding data). When the CMR spectrum of the compound was observed at both 25.2 MHz and 67.9 MHz without use of Cr(III) as a relaxation agent, the carbonyl carbon resonance was still a sharp singlet. The low temperature (–120 °C) spectrum of Ia exhibited three signals in the carbonyl region with a 1:1:4 area ratio. The area 4 resonance is probably an area 3 resonance overlapping an area 1 resonance. To obtain further information, we prepared the derivative $Fe_2(CO)_5PPh_3(\text{–}S\text{–}C(Ph){=}C(Ph)\text{–})$ (Ib) and determined its structure (see Figure 2) by single-crystal X-ray methods. Important distances in the molecule are indicated in Figure 3. A preliminary single crystal X-ray structure determination was reported for Ia [13]. After discussion with Dr. I. C. Paul [14], a further refinement of the data for Ia in our laboratory showed the structure of Ia to be very similar to that found for Ib, with the only difference being the

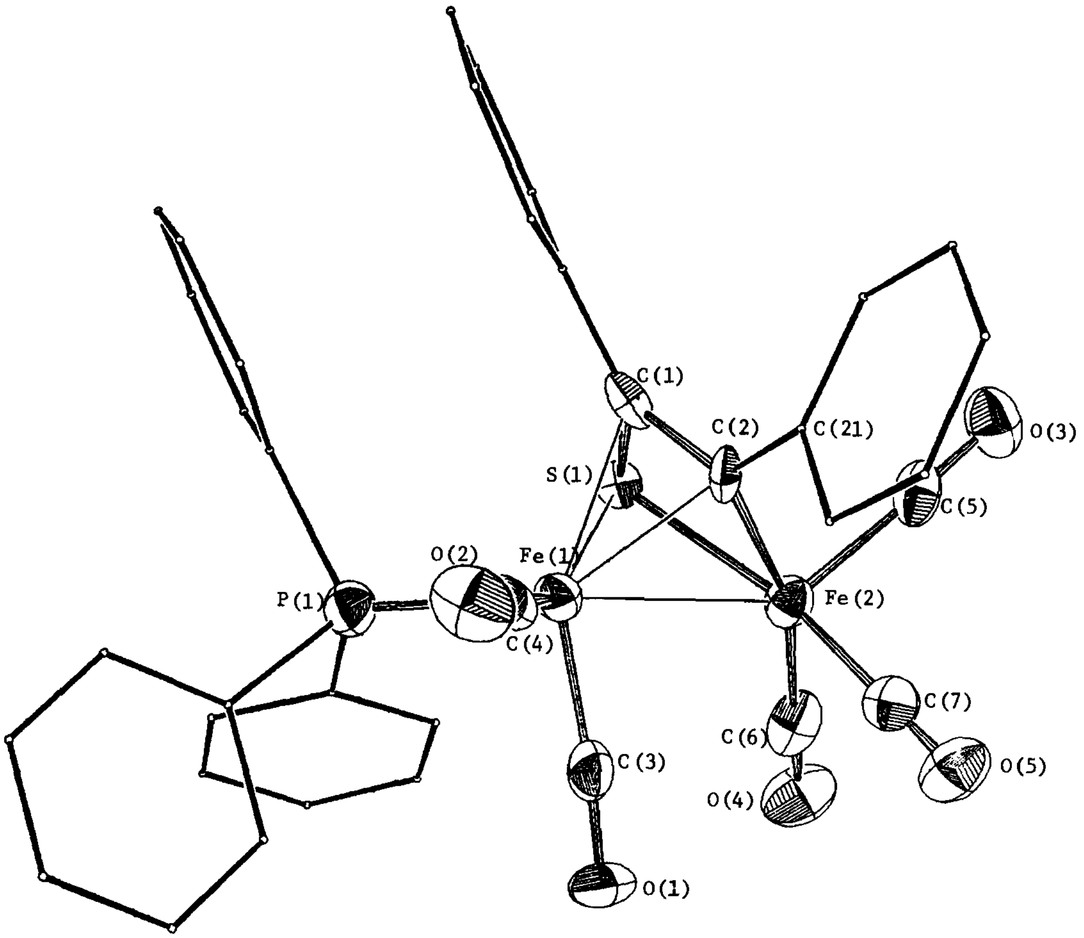


Figure 2. Solid state structure of $Fe_2(CO)_5PPh_3(-S-C(Ph)=C(Ph)-)$.

substitution of a carbonyl ligand with a triphenylphosphine group. It is interesting to note that in Ib the PPh_3 group resides on Fe(1), the "π-bonded" $Fe(CO)_3$ group. In the case of $Fe_2(CO)_5PPh_3(-C(Ph)=C(Ph)-C(Ph)=C(Ph)-)$, the phosphine was found to be attached to the ferrole ring iron [1].

The room temperature ^{13}C NMR spectrum of Ib contained three carbonyl signals in a 1:1:3 area ratio. The two unit area resonances exhibited $^{31}P-^{13}C$ coupling. At −120 °C the area three signal had split into two resonances at 210.3 ppm (area 2) and 204.5 ppm (area 1). These two signals did not display $^{31}P-^{13}C$ coupling. The carbonyl groups are not moving from Fe(1) to Fe(2) during this fluxional process.

$Fe_2(CO)_6(C_6H_4CH_2NR-)$ (IIa, R = CH_3; IIb, R = Ph)

In the ^{13}C NMR spectra of these derivatives at room temperature [25.2 MHz or 67.9 MHz, with or without added $Cr(acac)_3$] we observe one carbonyl carbon signal. Previously it had been reported that the room temperature spectrum of IIb contained two carbonyl signals of equal area separated by 0.4 ppm [15]. We obtained a sample of the compound from the author and with our instrumentation only one very sharp carbonyl carbon signal (in $CDCl_3$ solvent) was observed. We suggest that there must have been an instrumentation problem in the previous report.

At −120 °C the single carbonyl resonance separates into three signals each of equal area.

In the 100 MHz ^1H NMR spectrum of IIa, the methylene protons occur as a sharp area 2 singlet down to −120 °C.

Discussion

At low temperature the iron tricarbonyl group Fe(2) of Ia or Ib is static while iron tricarbonyl group Fe(1) is fluxional. This is similar to the carbonyl exchange pattern observed for most tricarbonylferrole–iron tricarbonyl compounds at low temperature [1, 2]. In many cases the replacement of a $>C=C<$ unit with an –S– unit leads to molecules with similar properties. At room temperature one or more new processes have become rapid on the nmr time scale for Ia and Ib which were not observed for

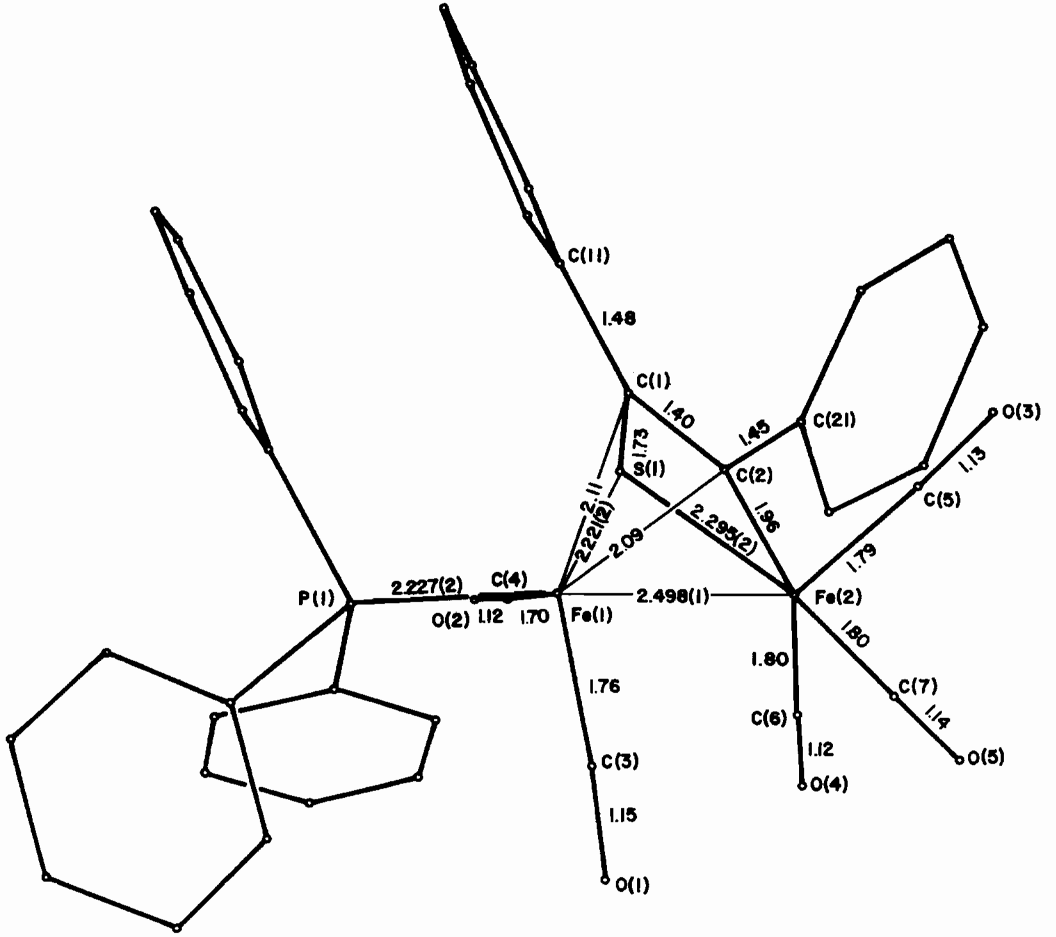


Figure 3. Important distances for $Fe_2(CO)_5PPh_3(\text{–}C(Ph){=}C(Ph)\text{–}S\text{–})$.

tricarbonylferrole–iron tricarbonyl compounds. At 30 °C only one CO signal is observed for Ia. We assume, based on the variable temperature NMR study of the phosphine-substituted derivative Ib, that there is only localized interchange of carbonyl groups on a given $Fe(CO)_3$ group for Ia. It is well known that there are small chemical shift changes of CO resonances with changes in temperature. This is clearly seen in the shielding data of the Fe(1) carbonyl carbons of Ib (Table II). As the temperature increases, the carbonyl carbons are more shielded. If only localized scrambling of carbonyl groups on Fe(1) and Fe(2) of Ia is occurring at 30 °C, there should be *two* observable CO signals. The Fe(1) signal would be at a slightly more shielded position than 209.6 ppm and the Fe(2) signal would be at a slightly more shielded position than 207.9 ppm (the average of 204.6, 209.6 and 209.63 ppm). Since only one carbonyl resonance was observed, a fluxional process of the L–L′ ligand must be occurring which in effect introduces a mirror plane between Fe(1) and Fe(2). One possible permutation process is outlined in Fig. 4. In this process, movement of the $-\underset{\text{Ph}}{C}{=}\underset{\text{Ph}}{C}-S-$ ligand (as shown in 4A and 4B) would result in an interchange of the bonding functions of the end atoms of the ligand. If the five coordinate forms 4C and 4D became operative, this would provide a route for Berry pseudo-rotation (as described in references 16–20) leading to permutation of the CO groups on a given $Fe(CO)_3$ group.

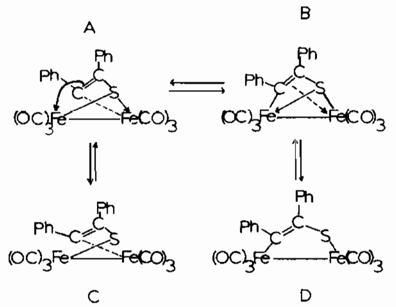


Figure 4. Possible mechanism for the fluxional processes of $Fe_2(CO)_6(\text{–}S\text{–}C(Ph){=}C(Ph)\text{–})$.

At −120 °C, which was the lowest temperature we were able to obtain, only three carbonyl carbon signals were observed for IIa and IIb. Six carbonyl carbon signals are expected for the static structure, based on the single crystal X-ray structure determination of the type IIb compound where there is a *p*-tolyl group on nitrogen [21]. This result may be due to the coincidental overlap of the expected six resonances to give three resolvable signals, or it may be due to a very facile fluxional process of the L–L′ ligand of the type described in Figures 4A and 4B which would generate a mirror plane between the two $Fe(CO)_3$ groups. It is apparent that at −120 °C there is no local carbonyl scrambling on each of the $Fe(CO)_3$ groups. At +30 °C, only a single carbonyl signal was observed for IIa and IIb. At this temperature local CO scrambling on both $Fe(CO)_3$ groups is occurring probably by Berry pseudorotation of five coordinate forms like 4C and 4D.

Acknowledgements

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