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TRANSITION-METAL COMPLEXES WITH σ-BONDED FLUORINE-CONTAINING GROUPS

VII *. INTRAMOLECULAR *cis-trans* ISOMERIZATION OF BIS-(PERFLUOROALKYL)IRON TETRACARBONYLS

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Summary

cis-$(C_nF_{2n+1})Fe(CO)_4$ ($n = 2$, 3, 4 and 6) complexes were studied via IR spectroscopy in the region of the ν(CO) bands. Stereochemical non-rigidity of these complexes in perfluorodecalin was found above 80–100°C. On the basis of the obtained kinetic and activation parameters of *cis-trans* isomerization, a conclusion was made about the intramolecular nature of the rearrangement process.

Introduction

Intramolecular *cis-trans* isomerization of carbonyl complexes of transition metals, $M(CO)_4L_2$ (M = Cr, Mo, W and $L = R_3P$ [2]), has been carefully examined. In most cases this process occurs without bond breaking (Bailar's twist [3] or related mechanisms [4,5]). Up to now, data on the mechanism and kinetics of *cis-trans* isomerization for $Fe(CO)_4L_2$ complexes are absent in the literature, except for a few studies [6,7], where the isomerization processes

$$cis\text{-}Fe(CO)_4I_2 \rightleftarrows trans\text{-}Fe(CO)_4I_2$$

$$cis\text{-}Fe(CO)_4(SiMe_3)_2 \rightleftarrows trans\text{-}Fe(CO)_4(SiMe_3)_2$$

were investigated. It was established that these intramolecular rearrangements are not accompanied by bond breaking.

To date, iron complexes with σ-bonded alkyl ligands have not been obtained due to their extreme instability [8]. Replacement of alkyl ligands with perfluoroalkyl radicals allows, in some cases, stable *cis* and *trans* $(R_F)_2Fe(CO)_4$ isomers to be

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* For part VI see ref. 1.

isolated. Heating *cis*-$(C_3F_7)_2Fe(CO)_4$ (in n-hexane solution or in the solid state at 110°C), as reported in [10], leads to the formation of *trans*-$(C_3F_7)_2Fe(CO)_4$. However, Hensley et al. [10] only ascertained the fact of a thermal *cis* → *trans* transition for the compound $(C_3F_7)_2Fe(CO)_4$.

The discovered reversibility of the *cis-trans* isomerization of these carbonyl complexes of iron enabled us to run a systematic kinetic investigation of this process for $(C_nF_{2n+1})_2Fe(CO)_4$ ($n = 2$, 3, 4 and 6) compounds. A possible mechanism of isomerization is discussed on the grounds of the kinetic and thermodynamic parameters obtained.

Experimental

Spectra. Infrared spectra (Table 1) were obtained on a Beckman M 4260 spectrophotometer which was calibrated in the region 2200–2000 cm^{-1} with carbon monoxide and polystyrene. Solution spectra were run in KBr cells with heptane and perfluorodecalin as solvents.

The ^{19}F NMR spectra were recorded at 188.28 MHz on a Bruker WP-200 spectrometer. Chloroform-d_1 was used as the solvent; $CFCl_3$ served as the internal reference. All ^{19}F signals are upfield from the internal reference.

Kinetic measurements. The isomerization reactions of $(C_nF_{2n+1})_2Fe(CO)_4$ ($n = 2$, 3, 4 and 6) were carried out in sealed KBr cells with 0.1 mm width in perfluorodecalin solutions, saturated with CO or N_2 after repeated freezing of the solvent in

TABLE 1

SPECTROSCOPIC DATA FOR THE $(C_nF_{2n+1})_2Fe(CO)_4$ COMPLEXES

Complex	$\nu(CO)$ (cm^{-1})
cis-$(CF_3)_2Fe(CO)_4$	2157m, 2098vs, 2082m [a]
(1)	2157m, 2100sh, 2098vs, 2082m [10] [a]
	2159m, 2102vs, 2085m [b]
cis-$(C_2F_5)_2Fe(CO)_4$	2155m, 2103vs, 2097vs, 2086m, 2080m [a]
(2)	2157m, 2106vs, 2100vs, 2088m, 2082m [b]
trans-$(C_2F_5)_2Fe(CO)_4$	2125w, 2097vs, 2065w [a]
(3)	2127w, 2100vs, 2068w [b]
cis-$(C_3F_7)_2Fe(CO)_4$	2154m, 2102vs, 2097vs, 2084m, 2097m [a]
(4)	2154m, 2102vs, 2097vs, 2084m, 2097m [10] [a]
	2150m, 2100vs, 2095vs, 2081m, 2078m [9] [c]
	2156m, 2104vs, 2099vs, 2087m, 2081m [b]
trans-$(C_3F_7)_2Fe(CO)_4$	2124w, 2096vs, 2064w [a]
(5)	2155vw(?), 2124w, 2096vs [10] [a]
	2127w, 2100vs, 2067w [b]
cis-$(C_4F_9)Fe(CO)_4$	2153m, 2102vs, 2097vs, 2084m, 2079m [a]
(6)	2155m, 2104vs, 2099vs, 2087m, 2081m [b]
trans-$(C_4F_9)_2Fe(CO)_4$	2124w, 2096vs, 2064v [a]
(7)	2126w, 2098vs, 2066w [b]
cis-$(C_6F_{13})_2Fe(CO)_4$	2154m, 2102vs, 2098vs, 2085m, 2080m [a]
(8)	2156m, 2104vs, 2099vs, 2086m, 2081m [b]
trans-$(C_6F_{13})_2Fe(CO)_4$	2127w, 2099vs, 2067vw [a]
(9)	

[a] Heptane solution. [b] Perfluorodecalin solution. [c] C_2Cl_4 solution.

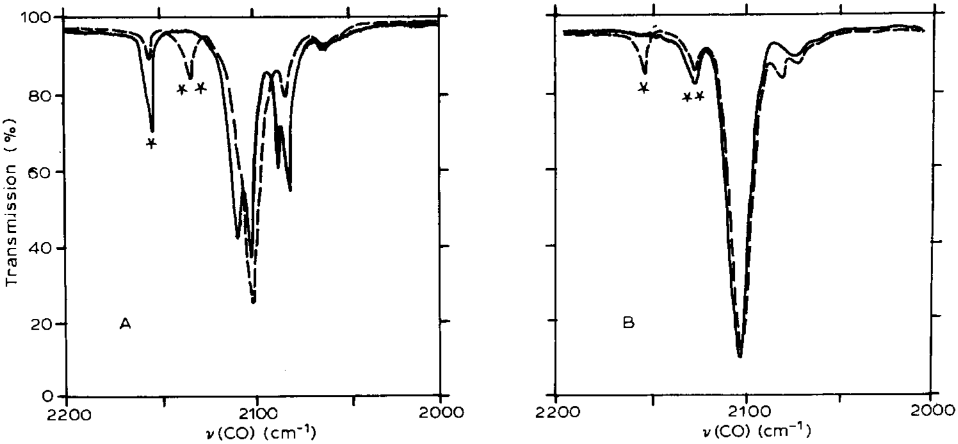

Fig. 1. Changes in ν(CO) absorptions of $(R_F)_2Fe(CO)_4$ during the approach to *cis-trans* equilibrium beginning with the pure isomer. A - *cis* isomer, B - *trans* isomer. Curve ——— corresponds to the spectrum of the pure isomer; curve — — — corresponds to the *cis-trans* mixture near equilibrium; (*, ** bands of *cis* and *trans* isomers, respectively, on which the kinetic measurements were run).

vacuum. The initial concentration of the *cis* (or *trans*) isomer was 9×10^{-2} mol l^{-1}. The rates of the *cis*-$(C_nF_{2n+1})_2Fe(CO)_4 \rightleftarrows$ *trans*-$(C_nF_{2n+1})_2Fe(CO)_4$ process were followed by observing the decrease in the peak intensity of the 2155 cm^{-1} band of the *cis* isomer and of the 2124 cm^{-1} band of the *trans* isomer with time. Figure 1 illustrates the changes in ν(CO) absorptions which take place as *cis* → *trans* and *trans* → *cis* equilibria are established after heating the initially pure isomer (the ν(CO) bands of the *cis* and *trans* isomers used in monitoring the kinetics are indicated by one and two asterisks, respectively). The rate constants $(k_1 + k_{-1})$ were calculated using the linear least-squares method for the first-order rate plots of $\ln(A_t - A_\infty)$ vs. time (~ 2155 cm^{-1} band) and $\ln(A_\infty - A_t)$ vs. time (~ 2124 cm^{-1} band), where A_t is the absorbance at time t, and A_∞ is the absorbance at equilibrium. The equilibrium constant for the *cis* ⇄ *trans* isomerization was determined spectroscopically employing ν(CO) bands at $t \to \infty$ mentioned above.

Preparation of compounds

cis-$(C_nF_{2n+1})_2Fe(CO)_4$ ($n = 1$, 2, 3, 4 and 6) compounds were obtained by the reaction of AgF with perfluoroalkyliron tetracarbonyl iodides [11]; *trans*-$(C_3F_7)_2Fe(CO)_4$ was synthesized by the method described in [12]. All other *trans* isomers were obtained by heating 0.5–1.5 mmol of *cis*-$(C_nF_{2n+1})_2Fe(CO)_4$ ($n = 2$, 4, 6) in an evacuated glass ampoule for 3–5 h at 100°C. Our attempt to isolate spectrally pure *trans* isomers with fractional sublimation of the isomer mixture (method [10]) failed. Separation of isomers was carried out chromatographically on a 15 × 1 cm silica gel column; the *trans* isomer was eluted with pentane and the *cis* isomer with freon-113. Pentane solutions of *trans*-$(R_F)_2Fe(CO)_4$ were evaporated at 0°C in vacuum (30 mmHg). The residue was sublimated at 40–50°C in vacuum (15 mmHg); *trans*-$(C_2F_5)_2Fe(CO)_4$ was recrystallized from pentane at −78°C. Product yields, melting points, elemental analysis data and ^{19}F NMR spectra data of *trans*-$(R_F)_2Fe(CO)_4$ are given in Table 2.

TABLE 2

PRODUCT YIELDS, MELTING POINTS, ELEMENTAL ANALYSIS DATA AND ^{19}F NMR SPECTRAL DATA OF *trans*-$(R_F)_2Fe(CO)_4$

R_F	Yield [a] (%)	M.p. (°C)	(Found (calcd.) (%))		Formula	Chemical shift δ(ppm) [b]		
			C	F		α-CF_2	Other CF_2	CF_3
C_2F_5	32 (70)	43	23.48 (23.68)	46.56 (46.80)	$C_8F_{10}FeO_4$	67.9s		83.95s
C_4F_9	50 (65)	70–72	23.65 (23.78)	56.27 (56.44)	$C_{12}F_{18}FeO_4$	63.5m	111.8m 125.5m	81.7m
C_6F_{13}	66 (73)	66–67	23.81 (23.84)	61.18 (61.29)	$C_{16}F_{26}FeO_4$	63.0m	110.9m 121.5m 123.25m 126.6m	81.3m

[a] The conversion of the *cis* isomer to the *trans* isomer is given in parentheses. [b] Abbreviations: s, singlet; m, complex multiplet.

Results and discussion

The infrared spectra of all the *cis* isomers exhibit five well-resolved bands in the terminal ν(CO) region (Table 1). According to Pitcher and Stone [9] and Hensley et al. [10], the infrared spectra of *cis*-$(C_2F_5)_2Fe(CO)_4$ and *cis*-$(C_3F_7)_2Fe(CO)_4$ are expected to show two bands of medium intensity at ∼ 2155 and ∼ 2080 cm^{-1} and a strong band at ∼ 2098 cm^{-1}. Additional bands at ∼ 2102 and ∼ 2079 cm^{-1} were explained by the presence in these compounds of two (or more) rotamers, which differ only in the relative conformations adopted by the mutually perfluoroalkyl groups. However, elongation on the perfluoroalkyl ligands would increase the number of rotamers and, hence, would result in the appearance of new additional bands. The infrared spectra of all the *cis* isomers, except *cis*-$(CF_3)Fe(CO)_4$ (see Table 1), are identical in the ν(CO) region, regardless of the length of the perfluoroalkyl groups and the solvents used. The symmetry of the *cis*-$(CHF_2CF_2)_2Fe(CO)_4$ complex, according to X-ray analysis [13], is not strictly C_{2v}. The reduction of molecular symmetry owing to the alteration of the angles between the neighbouring groups (deviation from strict C_{2v} symmetry) in *cis*-$(C_nF_{2n+1})_2Fe(CO)_4$ may lead to the realization of vibrations formally forbidden in infrared spectra. A similar situation was observed for the *trans* isomers of these complexes. The appearance of weak bands at ∼ 2150 and ∼ 2120 cm^{-1} (A_{1g} and B_{1g}, respectively) for compound 5 (Table 1), according to Hensley et al. [10] is caused by the reduction of symmetry from strict D_{4h} due to the lack of axial symmetry of the n-C_3F_7 group. It should be noted that the band at ∼ 2150 cm^{-1} is absent in the spectra of all the investigated *trans* isomers while the weak band at 2060 cm^{-1} is present in the spectra of these compounds. The most likely explanation is that Hensley et al. [10] used insufficiently pure compounds (see Experimental section of this work). As a result, in the spectrum of *trans*-$(C_3F_7)_2Fe(CO)_4$ a band appears at 2155 cm^{-1} caused by contamination with *cis* isomer, which has a medium-intensity band in this region. The appearance of the B_{1g} band in the spectrum of *trans*-$Fe(CO)_4I_2$, as shown by Pankowski and Bigorgne [6], is due to the molecular symmetry reduction $D_{4h} \rightarrow D_{2d}$ owing to the

TABLE 3

KINETIC PARAMETERS OF THE FIRST-ORDER REACTION $cis\text{-}(R_F)_2Fe(CO)_4 \rightleftarrows trans\text{-}(R_F)_2Fe(CO)_4$

Process	T (°C)	$(k_1+k_{-1})\times10^4$ (s^{-1})	K_{eq}	$k_1\times10^4$ (s^{-1})
1 $cis\text{-}(C_2F_5)_2Fe(CO)_4 \rightleftarrows trans\text{-}(C_2F_5)_2Fe(CO)_4$	80	0.8±0.1	6.0	0.7
	85	1.5±0.2	6.0	1.3
	90	3.8±0.1	5.9	3.2
	95	7.6±0.7	6.0	6.5
	100	13.9±1.8	6.0	11.9
$trans\text{-}(C_2F_5)_2Fe(CO)_4 \rightleftarrows cis\text{-}(C_2F_5)_2Fe(CO)_4$	100	12.79±0.05	6.0	10.68
2 $cis\text{-}(C_3F_7)_2Fe(CO)_4 \rightleftarrows trans\text{-}(C_3F_7)_2Fe(CO)_4$	80	1.6±0.1	9.2	1.4
	85	3.5±0.5	9.2	3.2
	90	10.1±1.0	9.3	9.1
	95	23.3±0.8	9.4	21.1
	100	47.1±1.8	9.3	42.5
3 $cis\text{-}(C_4F_9)_2Fe(CO)_4 \rightleftarrows trans\text{-}(C_4F_9)_2Fe(CO)_4$	80	2.1±0.1	10.7	1.9
	90	9.8±1.0	10.6	8.9
	100	35.7	10.7	32.6
4 $cis\text{-}(C_6F_{13})_2Fe(CO)_4 \rightleftarrows trans\text{-}(C_6F_{13})_2Fe(CO)_4$	80	1.1±0.1	9.5	1.0
	90	6.4±0.7	9.4	5.8
	100	20.4±2.0	9.7	18.5

alteration of the angles between the neighbouring groups. Hence, the bands at 2096 and 2064 cm^{-1} should be assigned to E and A_1 modes; the band at 2124 cm^{-1} corresponds to the B_1 mode.

Under heating, $cis\text{-}(C_nF_{2n+1})_2Fe(CO)_4$ in perfluorodecalin isomerized to a *cis-trans* mixture. The reaction solution remained clear, no decomposition having been registered during the rearrangement (spectroscopically, 100% of the starting material is accounted for in the isomeric mixture). The position of equilibrium (K_{eq}) was practically temperature-independent; besides, the transition from compound **2** to compound **4** was accompanied by an increase of K_{eq} with subsequent stabilization of this parameter for compounds with more elongated ligands (see Table 3, reactions 2–4).

The rates of isomerization were analysed as opposing first-order reactions (eq. 1), where $K_{eq} = k_1/k_{-1} =$

$$[trans\text{-}(R_F)_2Fe(CO)_4]_{eq}/[cis\text{-}(R_F)_2Fe(CO)_4]_{eq}$$

$$cis\text{-}(R_F)_2Fe(CO)_4 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} trans\text{-}(R_f)_2Fe(CO)_4 \qquad (1)$$

Since K_{eq} is much less then 100, k_1 being approximately (6–10)k_{-1}, both reactions must be considered. The values of the composite rate constants ($k_1 + k_{-1}$), determined for reaction 1 approached from either direction starting with the respective pure complex, are given in Table 3 for several temperatures. The individual rate constants k_1 and k_{-1} obtained from ($k_1 + k_{-1}$) values are also included in Table 3. Figure 2 illustrates a typical linear first-order rate plot, obtained over 3.5 half-lives.

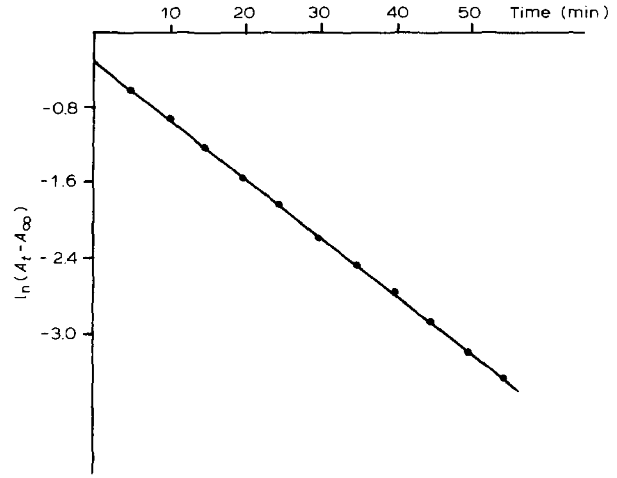

Fig. 2. Typical linear first-order rate plot of the reaction *cis*-$(C_3F_7)_2Fe(CO)_4 \rightleftarrows$ *trans*-$(C_3F_7)_2Fe(CO)_4$ (perfluorodecalin, 100°C).

Although both isomeric forms are thermally stable under the reaction conditions, the processes were carried out in CO atmosphere so that any formation of transition state complexes could be detected during the isomerization process. Unlike Mn carbonyl complexes [14], no transition complexes were recorded during the isomerization processes for all the compounds investigated. The rates of isomerization were the same in both CO and N_2 atmosphere. On the basis of these facts, it was concluded that in the case of the series $(C_nF_{2n+1})_2Fe(CO)_4$ ($n = 2$, 3, 4 and 6), *cis-trans* isomerization is a non-bond-breaking process like the intramolecular rearrangement of $Mo(CO)_4L_2$ complexes [15,17], which is also a non-dissociative process. The mechanism of intramolecular rearrangement based on Bailar's twist [3] or analogous rotation processes [4,5] is more typical for octahedral transition-metal complexes containing bidentate ligands. Therefore the energy barrier for complexes containing monodentate ligands should be expected to be high enough [2,4,5]. As can be seen from Table 4, which gives the thermodynamic parameters of reaction 1, the *cis-trans* isomerization reported herein is characterized by high activation energy values ($\Delta G^{\neq}$), which are slightly dependent on the length of the perfluoroalkyl radical.

TABLE 4

ACTIVATION PARAMETERS OF THE REACTION *cis*-$(R_F)_2Fe(CO)_4 \rightleftarrows$ *trans*-$(R_F)_2Fe(CO)_4$ (perfluorodecalin, 100°C)

Process	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J grad^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})
cis-$(C_2F_5)_2Fe(CO)_4 \rightleftarrows$ *trans*-$(C_2F_5)_2Fe(CO)_4$	156.6	117.2	113.0
trans-$(C_2F_5)_2Fe(CO)_4 \rightleftarrows$ *cis*-$(C_2F_5)_2Fe(CO)_4$	139.3	46.5	126.3
cis-$(C_3F_7)_2Fe(CO)_4 \rightleftarrows$ *trans*-$(C_3F_7)_2Fe(CO)_4$	188.0	193.4	109.3
cis-$(C_4F_9)_2Fe(CO)_4 \rightleftarrows$ *trans*-$(C_4F_9)_2Fe(CO)_4$	154.1	118.5	109.7
cis-$(C_6F_{13})_2Fe(CO)_4 \rightleftarrows$ *trans*-$(C_6F_{13})_2Fe(CO)_4$	157.8	157.8	111.4

The activation energy of the *trans-cis* process is about 13 kJ mol^{-1} higher than the $\Delta G^{\neq}$ value for the *cis-trans* isomerization process. This fact can be explained by the higher stereochemical stability of the *trans* isomer. The *cis-trans* equilibrium shift to the *trans* isomer is controlled by the entropy factor ($\Delta S^{\neq}$), which is lower for the *trans-cis* process than the *cis-trans* process (see Table 4).

The high positive $\Delta S^{\neq}$ values of the *cis-trans* isomerization are probably defined by two factors: the greater solvation of the more polar *cis* isomer and/or the increase of the degree of freedom for ligands in the less-hindered *trans* configuration [14,17]. One of the probable reasons of the stability of the *cis* isomer despite its steric factors may be the strengthening of the metal–fluoroalkyl linkage as a result of d_{π}–$\sigma^{\star}$ back-donation [13,16,18].

It is interesting to note the behaviour of *cis*-$(CF_3)_2Fe(CO)_4$. Above 80°C, the concentration of this compound decreases, but we could not record any trace of *trans*-$(CF_3)_2Fe(CO)_4$ in the solution. Probably the *trans* isomer was unstable and decomposed immediately after formation. However, this explanation does not rule out the possibility of dissociation processes accompanying isomerization. A high shift *cis-trans* equilibrium to the *cis* isomer has been recorded for many methyl-containing transition-metal carbonyl complexes [2,15], and was explained by the rise of stability of the *cis* isomer as a result of a decrease in steric factors. This is in agreement with the reduction of the K_{eq} values under transition from *cis*-$(C_3F_7)_2Fe(CO)_4$ to *cis*-$(C_2F_5)_2Fe(CO)_4$ (Table 3).

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