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^{1}H NMR STUDY OF THE REVERSIBLE *cis/trans* ISOMERIZATION OF $\{(\mu\text{-}CH_2)(\mu\text{-}CO)[\eta^5\text{-}C_5H_5Fe(CO)]_2\}$

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Summary

The *cis/trans* isomerization of the bridging methylene complex $\{(\mu\text{-}CH_2)(\mu\text{-}CO)[\eta^5\text{-}C_5H_5\text{-}Fe(CO)]_2\}$ was studied in solution by ^{1}H NMR spectrometry, using solvents with different polarities (acetone-d_6, chloroform-d_1 and benzene-d_6). Equilibrium constants and rate constants for the forward and reverse steps were measured between 278 and 323 K. Both reactions show first-order kinetics. A possible mechanism for the isomerization is proposed, involving the breaking of a Fe–Fe bond in the rate-determining step.

Introduction

The compound $Cp(CO)Fe(\mu\text{-}CO)(\mu\text{-}CHR)Fe(CO)Cp$ ($Cp = \eta^5\text{-}C_5H_5$; R = H (**1**)) and some of its alkyl derivatives ($R = CH_3$, n-C_3H_7) can be obtained by the reaction of $[CpFe(CO)(\mu\text{-}CO)]_2$ (**2**) with an appropriate alkylidenetriphenylphosphorane, $Ph_3P{=}CHR$ (Ph = phenyl; R = H, CH_3, n-C_3H_7) [1]. This reaction proceeds smoothly and with fairly good yields (up to about 50% for **1**). Other syntheses for **1** have been reported subsequently [2,3], although generally, with poorer yields and with the added disadvantage that **1** has to be separated from unchanged **2** by chromatography.

Both geometric isomers of **1** are formed during the reaction; they can be separated from each other and from other products by column chromatography at −20°C. After concentration of the respective solutions at low temperature, pure *trans*-**1** and *cis*-**1** can be crystallized out. At room temperature, the interconversion rate is significant, so that both isomers are always present in solution. Equation 1 represents the formation of **1**.

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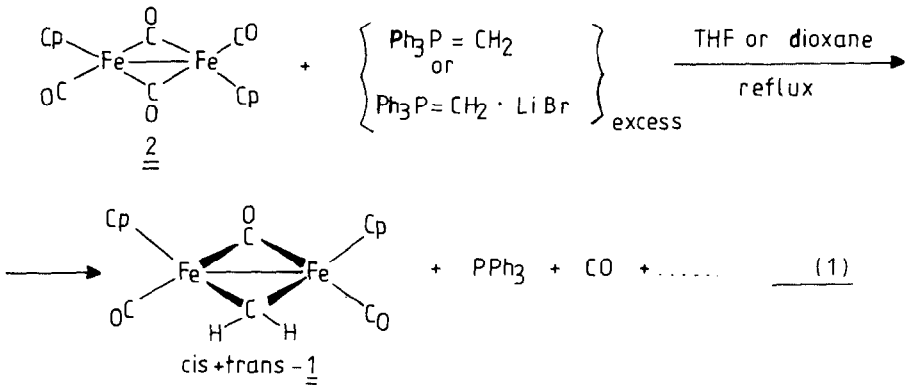


We wish to report here the kinetics of the *cis/trans* isomerization of **1**, as revealed by proton-nuclear magnetic resonance techniques (^{1}H NMR) at various temperatures and in various solvents, i.e. chloroform-d_1, acetone-d_6 and benzene-d_6.

Results

The ^{1}H NMR spectra [1] of *cis*-**1** and *trans*-**1**, hereafter called **C** and **T**, respectively, are simple, and lend themselves well to the kind of study we had in mind. At room temperature, both isomers are present in solution, and, in $CDCl_3$, for example, the following resonances can be observed (δ (ppm) TMS int. std.):

C	T
10.29 (s, 1H, μ-CH_2)	9.54 (s, 2H, μ-CH_2)
8.39 (s, 1H, μ-CH_2)	
4.74 (s, 10H, Cp)	4.76 (s, 10H, Cp)

Conveniently, the signals belonging to the CH_2-bridging group appear as singlets [4] within a range of 2 ppm.

There are two separate signals for **C** and only one signal for the two protons of the μ-CH_2 group in the *trans* compound. From their relative areas it was possible to determine equilibrium and rate constants for the isomerization at various temperatures and in the various solvents used. The relative area for **C** was taken as the integral sum for the peaks at around 10.3 and 8.4 ppm (there are slight variations in chemical shift depending on the solvent used), and the area for **T** was taken as the integral value for the peak at about 9.5 ppm. The expressions for the concentrations of **C** and **T** as molar fractions are:

$$X_C = A_C/(A_C + A_T); \qquad X_T = A_T/(A_C + A_T) \tag{2}$$

where:

A_C: relative total area of the μ-CH_2 signals in **C**.

A_T: relative area of the μ-CH_2 signal in **T**.

X_C, X_T: molar fractions of **C** and **T** respectively.

It follows, that the equilibrium constant K for the isomerization process can be written as:

$$K = X_T/X_C = A_T/A_C \tag{3}$$

TABLE 1

EXACT LOCATION OF THE μ-METHYLENE PROTONS (δ, ppm) IN VARIOUS SOLVENTS [5]

Solvent	C	T
chloroform-d_1, $CDCl_3$	10.29, 8.39	9.54
acetone-d_6, CD_3COCD_3	10.32, 8.26	9.58
benzene-d_6, C_6D_6	9.99, 8.52	9.49
methanol-d_4, CD_3OD	10.33, 8.34	9.61
CD_3COCD_3/C_6D_6 (1/2, v/v)	10.23, 8.44	9.56

TABLE 2

EQUILIBRIUM CONSTANTS K AT VARIOUS TEMPERATURES FOR THE ISOMERIZATION OF **1** [5]

T (K) [7]	$K \times 10^2$ [6]			
	acetone-d_6 ($K \pm 0.08 \times 10^{-2}$)	chloroform-d_1 ($K \pm 0.9 \times 10^{-2}$)	benzene-d_6 ($K \pm 0.05 \times 10^{-2}$)	methanol-d_4 ($K \pm 0.15 \times 10^{-2}$)
278	4.93	33.7	–	–
283	6.29	35.5	–	–
288	7.37	37.3	32.56	–
293	7.83	39.9	–	–
298	8.55	40.8	–	–
300	–	41.5	36.07	11.66
303	9.34	42.6	–	–
308	9.76	44.4	40.27	15.35
313	10.66	46.0	–	–
323	–	49.7	–	–

and the rate constant k can be determined by measuring the variations in the integral areas of the signals as a function of time (provided the reaction is slow enough at the working temperature).

Table 1 gives the exact location (δ values) of the μ-CH_2 signals in the various solvents used for this work and some others; Table 2 gives the calculated K values (according to eq. 3) at various temperatures in four solvents; in most cases, three measurements were made at each temperature, and their average used for determining the equilibrium constant.

From a plot of $-\ln K$ vs. $1/T$, the $\Delta H°$ and $\Delta S°$ values in the temperature range 283–313 K were determined for acetone-d_6, chloroform-d_1 and benzene-d_6. Measurements in methanol-d_4 and other solvents (or mixtures) were mostly unsatisfactory, due to the poor solubility of **1**. The values obtained are presented in Table 3.

TABLE 3

$\Delta H°$ AND $\Delta S°$ IN THE TEMPERATURE RANGE 283–313 K

Solvent	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})
acetone-d_6	12.3 ± 0.4	20.8 ± 1.0
chloroform-d_1	7.3 ± 1.8	16.9 ± 5.0
benzene-d_6	7.7 ± 0.4	17.2 ± 1.0

TABLE 4

RATE CONSTANTS FOR THE ISOMERIZATION[a]

Solvent	T (K)	$k_{obs}(\times 10^5)$ (s^{-1})	$k_a(\times 10^5)$ (s^{-1})	$k_b(\times 10^5)$ (s^{-1})
acetone-d_6	278	8.90 ± 0.80	0.42 ± 0.04	8.48 ± 0.90
	283	14.55 ± 1.05	0.86 ± 0.07	13.69 ± 1.16
	288	20.73 ± 1.82	1.42 ± 0.14	19.31 ± 1.91
	293	34.58 ± 2.87	2.51 ± 0.23	32.07 ± 2.99
chloroform-d_1	278	1.40 ± 0.17	0.35 ± 0.06	1.05 ± 0.17
	283	4.00 ± 0.28	1.05 ± 0.11	2.95 ± 0.32
	288	6.70 ± 0.64	1.82 ± 0.24	4.88 ± 0.65
	293	19.80 ± 3.04	5.64 ± 1.08	14.16 ± 2.70
benzene-d_6	288	15.97 ± 0.60	3.92 ± 0.15	12.05 ± 0.47
	300	87.00 ± 5.98	23.05 ± 1.62	63.95 ± 4.50
	308	117.40 ± 8.05	33.71 ± 2.36	83.70 ± 5.87

[a] Measurements in benzene-d_6 were at somewhat higher temperatures than those in acetone-d_6 and chloroform-d_1 because **C** is slightly less soluble in benzene.

The equilibration kinetics (eq. 4) were studied by monitoring the decrease of methylene proton signals due to **C** and the concomitant increase of the corresponding signal of **T** as a function of time. The data obtained fit eq. 5.

$$\mathbf{C} \underset{k_b}{\overset{k_a}{\rightleftharpoons}} \mathbf{T} \tag{4}$$

$$K = \frac{k_a}{k_b}; \quad k_{obs} = k_{eq} = k_a + k_b$$

k_{obs} is the observed equilibration rate constant.

$$\ln\{[(X_c)_t - (X_c)_{eq}]\} / \{[(X_c)_0 - (X_c)_{eq}]\} = -k_{obs}t \tag{5}$$

where $(X_c)_0$, $(X_c)_t$ and $(X_c)_{eq}$ denote, respectively, the initial concentration of **C**, the concentration at time "t", and the concentration at equilibrium [8].

First-order rate constants (k_{obs}) were determined by plotting $\ln[(X_c)_t - (X_c)_{eq}]$ against t [9], and are summarized in Table 4, together with the rate constants k_a and k_b defined in eq. 4. These plots were linear for three to five half-lives; thus, the results confirm that the *cis/trans* isomerization of **1** is an intramolecular process.

TABLE 5

ACTIVATION ENTHALPIES AND ACTIVATION ENTROPIES FOR THE ISOMERIZATION OF **1**

Activation parameter	Solvent		
	acetone-d_6 (278–293 K)	chloroform-d_1 (278–293 K)	benzene-d_6 (288–308 K)
$\Delta H_a^{\neq}$ (kJ mol^{-1})	77.3 ± 8.4	120.1 ± 23.3	79.5 ± 7.1
$\Delta S_a^{\neq}$ (J mol^{-1} K^{-1})	−69.0 ± 7.3	74.6 ± 14.2	−51.9 ± 2.1
$\Delta H_b^{\neq}$ (kJ mol^{-1})	56.3 ± 6.2	110.2 ± 21.4	71.8 ± 6.7
$\Delta S_b^{\neq}$ (J mol^{-1} K^{-1})	−119.8 ± 12.7	56.8 ± 10.9	−69.2 ± 1.3

From these data, activation enthalpies, $\Delta H^{\#}$, and activation entropies, $\Delta S^{\#}$, were obtained by plotting $-\ln(k_a h/kT)$ and $-\ln(k_b h/kT)$, respectively, against $1/T$ (h = Planck's constant; k = Boltzmann's constant).

Table 5 gives the activation parameters obtained from these plots for the isomerization reaction as described by eq. 4.

Discussion

It is now possible to discuss some mechanistic possibilities on the basis of the thermodynamical and kinetical data obtained.

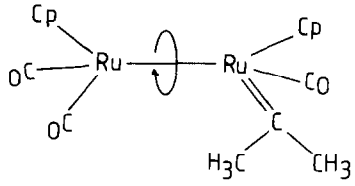
A comparison of the $\Delta H°$ and $\Delta S°$ values for the reaction in the different solvents (Table 3) shows an increase of both values when the isomerization takes place in acetone, whereas the values for chloroform and benzene are approximately equal. The larger $\Delta H°$ in acetone could be due to its better solvating of **C** because of its greater polarity, but then $\Delta H°$ in chloroform should be larger than in benzene (since the polarity of $CDCl_3$ is appreciably larger than that of C_6D_6), and this is not observed. Therefore acetone must have some important influence on an intermediate step in the isomerization, and solvation effects on the reactant seem not to be very significant.

The somewhat larger value of $\Delta S°$ in acetone supports this view if we interpret it in terms of a larger number of probable events. This number is proportional to the number of molecules involved in the isomerization process, and, since the reaction is intramolecular, the increase in $\Delta S°$ indicates the participation of solvent molecules in the overall mechanism. Solvation of the activated complex might be a first approximation to the special role of acetone in the isomerization reaction.

For a given temperature, the observed rate constant (k_{obs}, Table 4) is always larger in acetone; the fact that the reaction is faster in this solvent also suggests that there is stabilization of a polar intermediate, which diminishes the energy barrier and accelerates the reaction, but at the same time inhibits production of **T**, for now a stable intermediate is formed (a comparison of the values of the equilibrium constant K at a given temperature shown in Table 2 reveals that isomerization proceeds to somewhat lesser extent in benzene than in chloroform and to a markedly lesser extent in acetone). The stabilization of the intermediate, however, cannot be due exclusively to solvation, for in benzene also the reaction takes place significantly faster than in chloroform at a given temperature (Table 4). It would be unreasonable to assume that a polar intermediate can be better stabilized by an apolar solvent like benzene than by the more polar chloroform but the stabilization exists, and to such a degree that in benzene the production of **T** is also less than that in $CDCl_3$.

This evidence suggests clearly that there must be an intermediate, capable of being stabilized by acetone and, to a lesser degree by benzene, but not by chloroform. This in itself throws some light on the nature of the intermediate, and a possible mechanism for the isomerization reaction can now be considered.

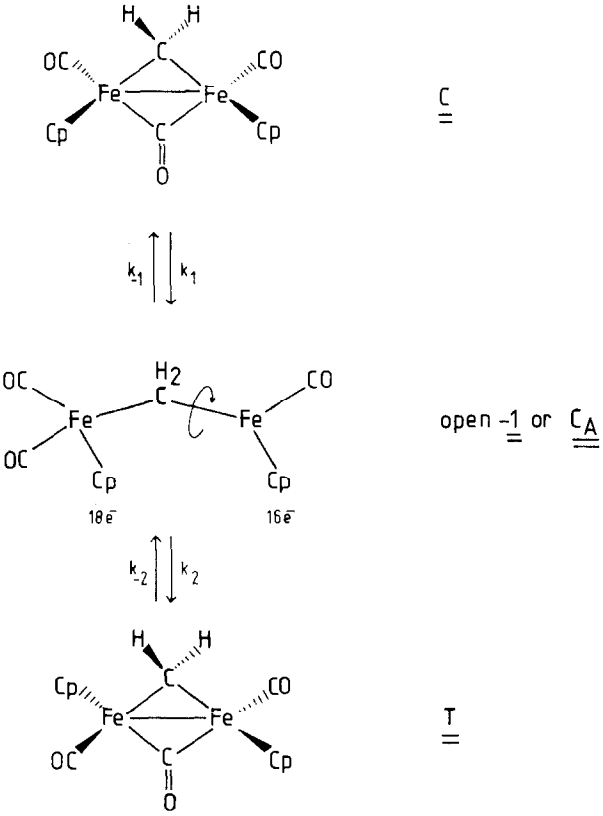
There have been relatively few studies of reaction mechanism of dinuclear μ-alkylidene species, although some possibilities have been suggested. For instance, Knox et al. [10] proposed an intermediate of the type "open-**3**" for the *cis/trans* isomerization of $\{(\mu\text{-CO})[\mu\text{-C}(CH_3)_2][CpRu(CO)]_2\}$ (**3**).



open - 3

Such an intermediate has thus a terminal carbene ligand, whereby both metal atoms retain an 18-electron cofiguration and there is free rotation around the Ru–Ru bond. In this case, an activation energy barrier of ca. 84 kJ mol^{-1} (20 kcal mol^{-1}) was estimated (from coalescence temperatures in ^1H NMR spectra of **3**), a value considered too high for isomerization by purely CO migration.

We believe that the intermediate in the case of the isomerization of **1** cannot be of the open-**3** type, since this would not explain the stabilizing effect of acetone and, especially, of benzene. The presence of an electron-deficient metal atom in the



SCHEME 1. A possible mechanism for the isomerization of **1**, showing the intermediate open-**1** (C_A) with one 16-electron iron atom.

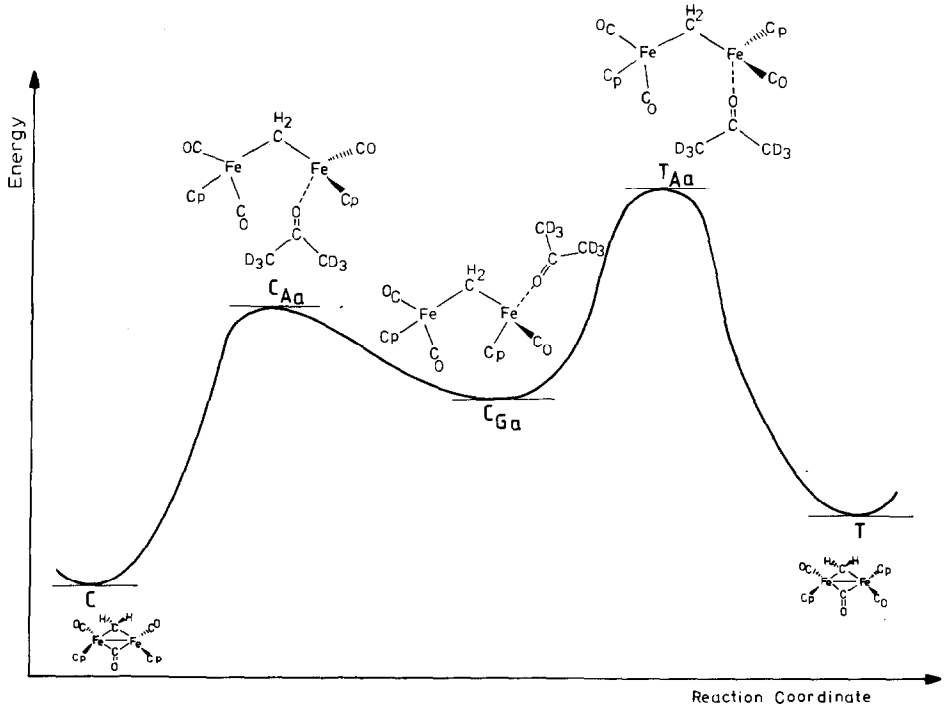


Fig. 1. Energy diagram for a possible isomerization mechanism in the coordinating solvent acetone-d_6, showing the stabilized intermediate $\mathbf{C_{Ga}}$.

intermediate seems likely, and Scheme 1 shows such a possible alternative reaction schema.

The 16-electron iron atom in the open-**1** ($\mathbf{C_A}$) intermediate can then be stabilized by σ-donation from lone oxygen pairs in the acetone molecule and, to a lesser degree but still effectively, by π-donation of two electrons from the benzene ring, as observed for the rather unstable complexes of the type $W(CO)_5$ (arene), where spectroscopic evidence strongly indicates that bonding involves the whole aromatic ring and not a fixed double bond [11].

The coordination of acetone and benzene to the intermediate is illustrated clearly by the $\Delta S^{\#}$ values for the forward and reverse steps (Table 5), these being negative in both cases. For chloroform, a non-coordinating solvent, positive $\Delta S^{\#}$ values are observed. Therefore, the reaction mechanisms must actually be different for the non-coordinating and coordinating solvents. Scheme 1 would be a reasonable mechanism for reaction in a non-coordinating solvent, where $\mathbf{C_A}$ (open-**1**) represents the sterically most stable conformation for the species, not necessarily a *cis* or *trans* form.

For the coordinating solvents, however, a possible mechanism is represented by the following sequence:

$$\mathbf{C} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{C_{Aa}} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathbf{C_{Ga}} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathbf{T_{Aa}} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \mathbf{T} \qquad (6)$$

where:

$\mathbf{C_{Aa}}$,$\mathbf{T_{Aa}}$: open forms of **C** and **T**, respectively, which are immediately coordinated by a solvent molecule. They are activated complexes.

$\mathbf{C_{Ga}}$: an open species which has undergone some rotation around the Fe–CH_2–Fe axis to acquire the sterically most stable conformation. A solvent molecule is coordinated to it, and it represents a stabilized intermediate.

The mechanism represented by eq. 6 is shown as an energy diagram in Fig. 1.

The activation parameters found for the reaction in acetone-d_6 (Table 5) are very illuminating. While activation enthalpies for both reaction directions ($\Delta H_a^{\neq}$ and $\Delta H_b^{\neq}$ resp.) are similar the activation entropies differ considerably, and are thus largely responsible for the differences between k_a and k_b (Table 4). These facts point to bond-breaking as the rate-determining step, namely $\mathbf{C} \rightarrow \mathbf{C_{Aa}}$, and, by the principle of microscopic reversibility, $\mathbf{T_{Aa}} \leftarrow \mathbf{T}$ (eq. 6). For the other two solvents, activation enthalpies are still similar, but there is no marked difference between the $\Delta S_a^{\neq}$ and $\Delta S_b^{\neq}$ values; thus, rate constants for both reaction directions do not differ as markedly as in acetone-d_6.

In order to form the activated complexes $\mathbf{C_{Aa}}$ and $\mathbf{T_{Aa}}$ (or the open form $\mathbf{C_A}$) – two bonds must break: the μ-CO–Fe bond and the Fe–Fe bond. Since, however, the opening of CO bridges in solution is known to take place readily enough (requiring an activation enthalpy of only 27 ± 4 kJ mol^{-1} in the case of **2** [12], it must be the breaking of the Fe–Fe bond which is rate-determining in the isomerization of **1**. The $\Delta H^{\neq}$ values in Table 5 are comparable to the values of 96 kJ mol^{-1} suggested by Cutler et al. [13] for the activation enthalpy in the dissociation of the Fe–Fe bond of **2** in solution.

Experimental

All equilibrium constants as well as rate constants were determined by ^{1}H NMR spectroscopy (in the various deuterated solvents used for this work) with TMS as internal standard, through evaluation of the peak integrals for the μ-CH_2 signals (Table 1). All samples were prepared by dissolving 11–12 mg (ca. 0.035 mmol) of *cis*-**1** ($\geqslant$ 98% pure) in 0.45–0.49 ml of the corresponding deuterated solvent (Merck). {[CpFe(CO)]$_2$(μ-CH_2)(μ-CO)} (**1**) was prepared by the procedure described previously [1]; *cis*-**1** was purified from the secondary products *trans*-**1** and PPh_3 by column chromatography at -20°C, and then recrystallized from diethyl ether/n-pentane at dry ice temperature.

TABLE 6

EMPIRICAL PARAMETERS FOR NMR MEASUREMENTS

Solvent	PW (μs)	01 (Hz)	SW (Hz cm^{-1})	NS	AQT (ms)	S/N[a]
CD_3COCD_3	3.5	6700	25	100	3407.0	117
$CDCl_3$	3.5	6500	30	100	6000.0	120
C_6D_6	3.5	6300	25	100	4096.0	115
CD_3OD	3.5	6650	25	100	3407.0	37

[a] Average value in the range 8–11 ppm.

A Bruker WP-80 NMR spectrometer, fitted with a Bruker B-St-100/700 temperature control unit, was used.

The spectrometer was adjusted in such a way as to obtain the most satisfactory compromise between the best S/N (signal/noise) relationship and duration time of the experiment (ca. 10–15 min, depending on the solvent used). The equipment variables were then kept constant for all measurements in a given solvent. The magnet temperature (299 K), initial frequency, and the number of memory bytes for data acquisition (8 Kbytes) were kept constant throughout the work. Table 6 gives the empirical parameters for the NMR measurements (PW = pulse width; off-set (01); SW = spectral width; NS = number of scans; AQT = acquisition time; S/N = signal to noise ratio)

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4 However, under certain conditions the μ-CH_2 protons of **C** appear as two doublets, J 0.6 Hz. See also ref. 2.
5 For conditions of measurement, see Experimental.
6 Average error values are given for each set of K values.
7 The error in the temperature measurement was taken as ± 1 K, according to the specifications of the equipment used.
8 In all cases, equilibrium was considered established when no observable change in the integral values for the μ-CH_2 signals could be detected any more between successive measurements.
9 Average error values for X_c: CD_3COCD_3 ± 0.0007; $CDCl_3$ ± 0.0034; C_6D_6 ± 0.0006.
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