Vibrational spectra and structure of "staircase" carbonyl π-complexes of transition metals

2. Rotational isomerism

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FTIR spectra have been studied for "staircase" cyclopentadienyl complexes containing two or three metal carbonyl fragments bound by the metal—carbon bond $Cp(CO)_2Fe—CpmMn(CO)_3$ (**1**), $Cp(CO)_2Fe—CpmFe(CO)_2CH_2Ph$ (**2**), $Cp(CO)_2Fe—Cpm(CO)_2Fe—CpmMn(CO)_3$ (**3**), $Cp(CO)_2Mo—Cpm(CO)_2Fe—CpmMn(CO)_3$ (**4**), $Cp(CO)_3W—Cpm(CO)_2Fe—CpmMn(CO)_3$ (**5**), $Cp(CO)_2Fe—Cpm(CO)_2Fe—BmCr(CO)_3$ (**6**), $Cr(CO)_3Bm—CpmFe(CO)_2CH_2Ph$ (**7**), where Cp = η^5-C_5H_5, Cpm = η^1:η^5-C_5H_4, Bm = η^1:η^6-C_6H_5. Temperature-dependent FTIR spectra were measured in *n*-pentane solutions over a wide temperature range and in the low-temperature solid matrices of argon and nitrogen. Rotamers, formed due to rotation about the metal—carbon σ-bond, were found in solutions and matrices. A molecular mechanics calculation of **1** proved the possibility of such rotation.

Key words: infrared spectra, rotational isomerism, π-complexes.

In our previous paper[1], IR spectra in the νCO range were studied for di- and tri-nuclear complexes

$Cp(CO)_2Fe—CpmMn(CO)_3$ (**1**),
$Cp(CO)_2Fe—CpmFe(CO)_2CH_2Ph$ (**2**),
$Cp(CO)_2Fe—Cpm(CO)_2Fe—CpmMn(CO)_3$ (**3**),
$Cp(CO)_2Mo—Cpm(CO)_2Fe—CpmMn(CO)_3$ (**4**),
$Cp(CO)_3W—Cpm(CO)_2Fe—CpmMn(CO)_3$ (**5**),
$Cp(CO)_2Fe—Cpm(CO)_2Fe—BmCr(CO)_3$ (**6**),

where Cp = η^5-C_5H_5, Cpm = η^1:η^5-C_5H_4, Bm = η^1:η^6-C_6H_5. It was found that the spectra may be considered a superposition of the spectra of individual metal carbonyl fragments with a small vibrational coupling between the νCO modes. The mutual electron effect of the neighbouring groups is important. The fragments linked by a metal atom are strong electron donors relative to the other part of the molecule, and those linked by the carbon atom of the π-cycle are strong electron acceptors.

The subject of this paper is the rotational isomerism that might occur due to rotation about the metal—carbon σ-bond. X-ray data for complexes **1** and **2**[2—5] suggest such a possibility because these complexes exist as different conformers in the solid state. In one case, the cycles are nearly orthogonal, in the other, they are nearly parallel. In solutions, the conformers could exist in equilibrium if their energy difference is not large (1—5 kJ/mol) and the barriers of the rotation are not very high (no more than 30 kJ/mol). In this case, the conformer ratio in solutions should be temperature dependent.

To elucidate conformational equilibria in solutions, we studied temperature dependent IR spectra and performed a molecular mechanics calculation for complex **1**.

Experimental

All complexes were prepared according to known procedures[2—6]. IR spectra were recorded on a Bruker IFS-25 spectrometer with a resolution of 2 cm^{-1} and a Bruker IFS-113v spectrometer with a resolution of 1 cm^{-1}. A Zeiss cryocell cooled with liquid nitrogen was used for recording the low-temperature spectra of solutions. The spectra of the solid matrices were measured with a Displex closed cycle cryogenic system.

The calculation of rotamers for complex **1** (Fe, Mn) was carried out by the atom—atom potential method[7] using the

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Table 1. Carbonyl stretching frequencies (cm^{-1}) in *n*-pentane solutions

Complex	Fragment		
	$Cp(CO)_nM—$ M = Fe (*n* = 2) M = Mo (*n* = 3)	$Cpm(CO)_2Fe—$	$CpmMn(CO)_3$
(Fe, Mn) (**1**)	2037, 1988 (2040, 1992)*		2010 1934 (1921)
(Fe, Fe) (**2**)	2035, 1986	1995, 1938 (1990, 1944)	
(Fe, Fe, Mn) (**3**)	2042, 1991	2023, 1968 (2018, 1963)	2005, 1929 (1919) (1911)?
(Mo, Fe, Mn) (**4**)	2043, 1965	2026, 1957 (2021, 1946)?	2007 1930 (1919)
(W, Fe, Mn) (**5**)	2047, 1963, 1932 (2041)	2025, 1947	2011 1894 (2008)
(Fe) (**8**)	2011, 1960		

* The frequencies of the less stable conformer are given in parentheses.

NONVPOT program developed in this Institute. The parameters of the potential "6—exp":

$$U = -A/R^6 + B\exp(-CR)$$

for non-metal atoms were taken from Ref. 8 For the iron and manganese atoms, several parameters versions were tried, simulating various values of attraction and repulsion. The role of the Fe and Mn atoms did not appear to be significant, and only their electrostatic interaction with other atoms is important. For this reason, one of the parameter sets was used for obtaining the presented data (the parameters were taken as equal for Fe and Mn): A = 400.0, B = 90000.0, and C = 4.2 kcal/mol. The initial geometry was taken from Ref. 4. The rotation angle about the Fe—C bond was varied stepwise (steps of 6°); for each torsional angle value, the sub-optimization of the cyclopentadienyl and carbonyl group positions was performed.

Results and Discussion

The number of νCO bands in the spectra of solutions of **1**—**6** in CH_2Cl_2 are in line with that expected on the basis of the local symmetry of each metal carbonyl center[1]. If a mixture of rotamers exists in the solution, their νCO bands should be somewhat different in frequencies causing the splitting of some bands in the spectrum. At low temperatures, however, some bands become merely asymmetrical.

It is known[9,10] that the half width of νCO bands in IR spectra strongly depends on the nature of the solvent. In nonpolar solvents, where the interaction between a solvent and a solute is minimal, bands become narrower and in some cases, nearby bands might be resolved. Indeed, for compounds **1**—**6**, a number of bands that seemed single in a CH_2Cl_2 solution appear to be split into doublets in the spectra of an *n*-pentane solution (Table 1). Thus for complex **1** (Fe, Mn) (Fig. 1, *a*), both bands assigned to the $Fe(CO)_2$ fragment as well as the *E* band of the $Mn(CO)_3$ fragment are split. The number of

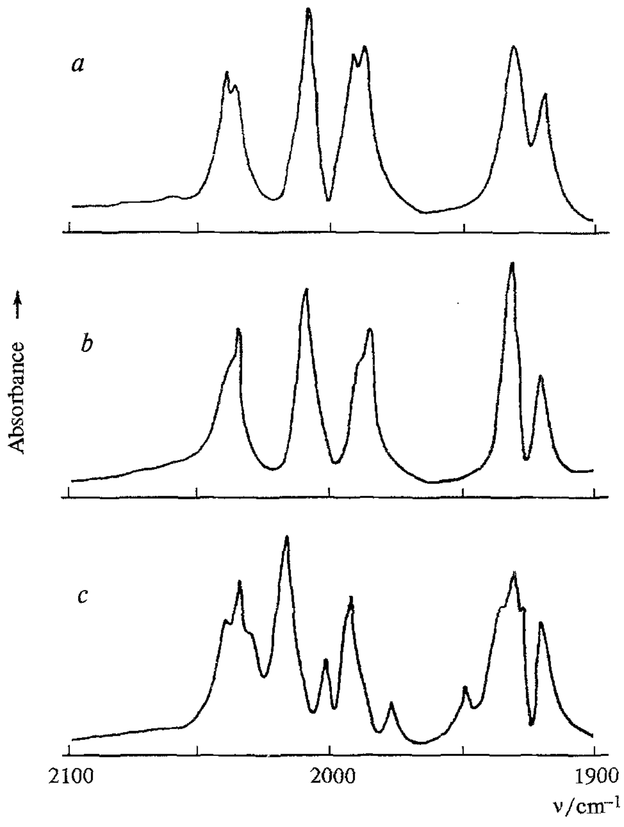

Fig. 1. IR spectra of complex **1** (Fe, Mn) in the νCO region: (*a*) in pentane solution at ~20°C; (*b*) in pentane solution at −90°C; (*c*) in the matrix of solid argon.

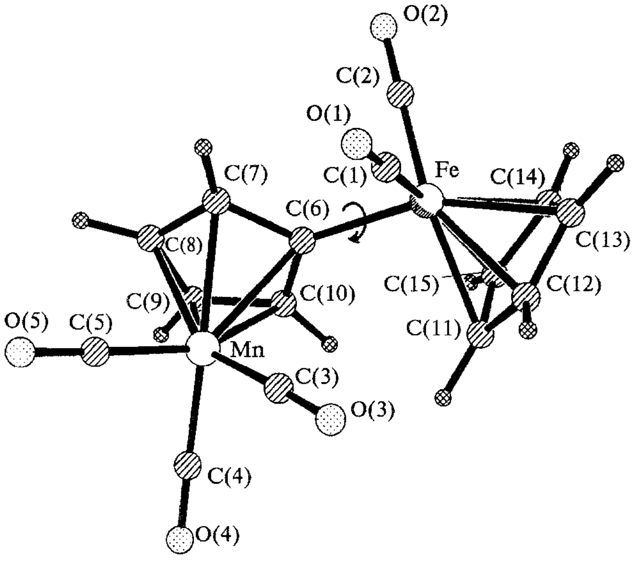

Fig. 2. Initial geometry and the atoms numbering for complex **1** (Fe, Mn).

bands in the spectra is much larger than expected even if the degeneracy breaks down. This situation can be rationalized if the presence in solutions of several rotamers is assumed.

An atom-atom potential calculation of complex **1** (Fe, Mn) confirms the rotational isomerism. The initial geometry of the complex and the atom numeration used are given in Fig. 2. The dependence of the intramolecular potential on the torsional angle for nonvalent interactions φ = C(1)—Fe—C(6)—C(10) is given in Fig. 3. The results of the model calculation are presented in Table 2. They show that at least four conformers may exist. Two of them, with torsional angles of −8.4 and 159.6°, correspond to rotamers containing the mutually orthogonal cyclopentadienyl rings; the others, with torsional angles of −128.4° and +45.6°, correspond to conformers with minimal dihedral angles between the rings. For every pair of angles, the difference in azimuth angles of the rotation about the Fe—C(6) axis is approximately 180°. X-ray data show that in the crystal, a conformer with a torsional angle of 33.6° exists (the angle between the ring planes is 98°); this torsional angle value is close to that calculated for the most stable conformer. However, the calculation indicates that the energy differences between conformers are rather small and equal to 0.1, 0.05, and 0.32 kcal/mol, respectively, taking the energy of the most stable conformer as a zero energy. Hence, all possible conformers may in principle be in equilibria at room temperature.

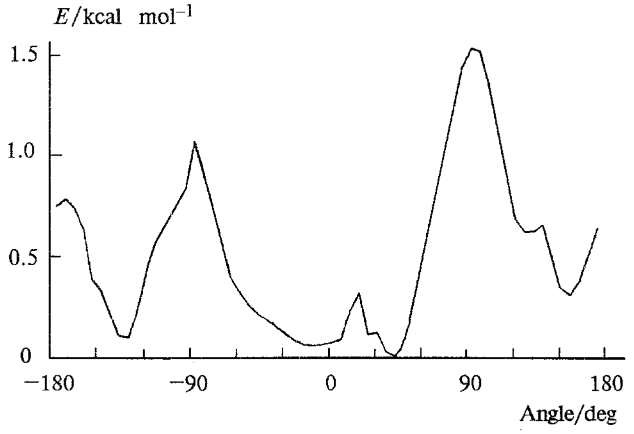

Fig. 3. Dependence of the intramolecular non-valent interaction potential on the dihedral angle C(1)—Fe—C(6)—C(10) for complex **1** (Fe, Mn).

Table 2. The results of the molecular mecanics calculation of $Cp(CO)_2FeCpmMn(CO)_3$

Dihedral angle C(1)FeC(6)C(7) (deg)	E kcal mol^{-1}	Barrier of rotation	ΔE kcal mol^{-1}
−170.4	5.24 (max)	0.68	
−128.4	4.56 (min)	0.97	0.1
−86.4	5.53 (max)	1.02	
−8.4	4.51 (min)	0.28	0.05
+21.6	4.79 (max)	0.33	
+45.5	4.46 (min)	1.54	0
+93.6	6.00 (max)	1.22	
+159.6	4.78 (min)	0.46	0.32
−170.4	5.24 (max)		

For complex **1** (Fe,Mn), the frequencies in the spectrum of a pentane solution are up-shifted by 5—18 cm^{-1} as compared to those in the spectrum of a CH_2Cl_2 solution. For the $Fe(CO)_2$ fragment, two doublets are observed at 2040, 2037 and 1992, 1988 cm^{-1} with a splitting of 3—4 cm^{-1}. The A_1 band (2010 cm^{-1}) of the $Mn(CO)_3$ fragment remains unchanged, but the E mode exhibits a doublet of 1934, 1921 cm^{-1}. Doublet components have different intensity, for this reason, the splitting of bands is not caused by the degeneracy break-down but might be caused by the presence of rotamers in the solution. After cooling to −90 °C (Fig. 1, *b*), the intensity ratio in doublet components is changed. This change is not large but is clear taking into account the small energy difference between isomers. The relative intensities of low-frequency components of the doublets assigned to the $Fe(CO)_2$ group increase; for the $Mn(CO)_3$ group, the intensity of the 1934 cm^{-1} band increases with respect to that of the 1921 cm^{-1} band. This means that the bands at 2040, 2010, 1992, and 1921 cm^{-1} belong to the less stable conformer, and the bands at 2037, 1988, and 1934 cm^{-1} belong to the more stable one (the shift of the 2010 cm^{-1} band after a change in the conformation is small). After a raise in the temperature, the initial intensity ratio is restored. Thus, unlike the conclusion made earlier for CH_2Cl_2 solutions, the vibrational coupling between carbonyl groups at different metal atoms does influence νCO frequencies, thus allowing us to distinguish rotamers, for which this coupling is different due to different spatial arrangement of the CO groups. These shifts are small as compared to those caused by the substituent mutual electronic effect, and in CH_2Cl_2 solutions, they are within the limits of the band width. It is remarkable that the low-frequency shift of the band maxima for CH_2Cl_2 solutions following a drop in temperature may also result from the change in the rotamer ratio in solutions. It is clearly seen in the spectrum of the model compound $Cp(CO)_2FeCH_2Ph$ (**8**) in a pentane solution that the νCO^{as} at 1961 cm^{-1} is broadened and has a shoulder at 1965 cm^{-1}, while the band at 2011 cm^{-1} is also slightly asymmetrical from the low-frequency side. This picture may be due to the rotation of the benzyl substituent about the Fe—C bond.

In the spectrum of **2** (Fe, Mn), the bands are also shifted by 7—9 cm^{-1} as compared to those for CH_2Cl_2 solutions, and six bands are observed instead of four. The intensities of the bands at 1990 and 1944 cm^{-1} are decreased upon cooling, and therefore these bands may be assigned to the less stable conformer. The doublet 1944/1938 cm^{-1} belongs to the $Cpm(CO)_2FeCH_2Ph$ fragment. Since the rotation about the Fe—CH_2 bond in the model compound $Cp(CO)_2FeCH_2Ph$ (**8**) leads only to some broadening of CO bands, the observed splitting of 6 cm^{-1} is caused by the presence of rotation about the Fe—C (ring) bond. The assignment of the 1990 cm^{-1} band is ambiguous. The latter could belong to a component of the doublet of either the νCO^{as} of the "upper step" $Fe(CO)_2$ or to the νCO^{s} of the "lower step". In both cases, the splitting is 4—5 cm^{-1}. Unlike in **1**, no splitting of the νCO^{s} of the "upper" $Fe(CO)_2$ fragment is observed.

For complex **3** (Fe, Fe, Mn), rotation is possible about two Fe-ring σ-bonds resulting in a sharp increase in the number of conformers. However, clear-cut splitting of 5 cm^{-1} is observed only for two bands of the central $Fe(CO)_2$ group, while the bands of the terminal $Fe(CO)_2$ group are somewhat broadened. Like for complex **1**, the high frequency A_1 band of the $Mn(CO)_3$ fragment is not split but the E band is split into three and more components. This favors the isomerism arising from the rotation about the Fe—C_5H_4Mn bond. Unlike **1**, the isomer with higher νCO values is more stable.

For complex **4** (Mo, Fe, Mn), the bands of the $Fe(CO)_2$ and $Mn(CO)_3$ groups are split and their intensities are temperature dependent, which means that the rotation about the Fe—C_5H_4 bond also occurs.

The spectrum of complex **5** (W, Fe, Mn) looks different when compared to that of **4**. The splitting is observed for the bands of the $W(CO)_3$ and $Mn(CO)_3$ groups and is not pronounced for the $Fe(CO)_2$ group. Moreover, a new broad band at 1890 cm^{-1} appears in the spectrum. This band is absent in the spectrum of a CH_2Cl_2 solution and is much more down-shifted than in the spectra of other complexes. The bands in the range of 1900—1950 cm^{-1} are difficult to assign but it is evident that **5** exists as a mixture of more than two conformers, in particular, the rotation might occur not only about the Fe-ring σ-bond but about the W-ring σ-bond as well.

It is of interest to compare the spectra of solutions with those of low-temperature solid matrices. Since the matrix is formed from the gas phase, which is rapidly cooled to a temperature of about 20 K, the conformers existing in the gas phase might be expected to be "frozen," their ratio being close to that in the gas phase. The bands in the spectra of inert matrixes at low temperature are narrow and therefore the bands are well resolved. The spectrum of **1** in solid nitrogen solution (Fig. 1, *c*) is very much similar to that in the liquid pentane solution (Fig. 1, *a*, *b*). Taking apart two bands (2060 and 2140 cm^{-1}) probably associated with the complex decomposition, the spectrum of the matrix is practically identical to the spectrum of a pentane solution, though the contour of the E band of $Mn(CO)_3$ is more complicated. Such similarity allows us to suppose that the band splitting in the matrix is not associated with specific matrix effects but is caused by the presence of a mixture of rotamers. This is also confirmed by the fact that the band intensity ratio in the matrix spectrum depends on conditions of matrix preparation (evaporation temperature, deposition rate, *etc.*), that is, on conditions leading to the shift of the conformational equilibrium in the gas phase. The complex contour of the E band of $Mn(CO)_3$ can be caused by both matrix effects and degeneracy break-down in the solid phase.

The spectrum of **1** in a solid argon matrix is even more complicated. Most bands exhibit additional splitting into several peaks separated by 2—4 cm^{-1} due to matrix effects. Moreover, the band narrowing in the matrix spectra may allow more than two conformers to be distinguished. An atom-atom potential calculation predicts the rotational isomerism and close values of conformer energies.

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