



IR study of rotational isomerism in dirhenium and diruthenium complexes of the ferrole type

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Abstract

A novel type of rotational isomerism was found in binuclear dirhenium complex of ferrole type $\text{Re}_2(\text{CO})_7(\text{C}_8\text{H}_7\text{Ph}_2\text{Fc}_2)$ (**II**) by Fourier transform IR spectroscopy in a wide temperature range (165–293 K) in pentane and liquid xenon solutions. The conformers result from internal rotation of a metal carbonyl moiety about the multicentred bond involving another metal carbonyl fragment. According to IR and Raman spectroscopy, the diruthenium complex $\text{Ru}_2(\text{CO})_6\{\text{C}_4\text{Fc}_2(\text{C}\equiv\text{CFc})_2\}$ (**III**) exists in the solid state and in solution as two different conformers. In the solid state the ‘non-sawhorse’ conformation with the semibridging carbonyl group was found, which transforms in solution to the conformation containing only terminal carbonyl groups. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: IR spectroscopy; Metal carbonyls; Rotational isomerism; Rhenium complexes; Ruthenium complexes; Metallacycles

1. Introduction

Internal rotation of various groups about different type bonds is a well-known phenomenon in organic chemistry. However, for organometallic compounds, rotation about the bonds involving the transition metal atom, has not often been observed. Only few examples of the internal rotation in solution are known, viz., about the metal–element bond [1,2], about the metal–carbon σ -bond [3,4], and about the metal–metal bond [5,6]. For π -complexes of the ferrocene type, the transition between two conformations, staggered and eclipsed, has been found by solid state NMR spectroscopy [7]. These conformers are formed due to internal rotation about the multi-centred metal– π -ligand bond, however, in solution these rotamers were not detected. The only example of internal rotation about the multicentred π -bond in solution was reported for some diene- $\text{Fe}(\text{CO})_3$ complexes [8]. However, in this case the rotation of the $\text{Fe}(\text{CO})_3$ moiety about the multi-centred bond is degenerate and individual rotamers cannot be observed in solution, therefore in

the IR spectra at room temperature (r.t.) only two broadened $\nu(\text{CO})$ stretching bands were observed.

In this paper we report a novel type of rotational isomerism associated with internal rotation of a metal-carbonyl fragment about the multi-centred π -bond found in binuclear rhenium complex of the ferrole type by IR spectroscopy. Another example of this type isomerism was found on going from the solid state to solution in binuclear ruthenium complex of the ferrole type. These compounds resulted from the reactions between $(\text{CO})_5\text{ReC}\equiv\text{CPh}$ or $\text{Ru}_3(\text{CO})_{12}$ with acetylene derivatives and can be considered as intermediates of transition metal promoted oligomerization/annulation of alkyne molecules. For this reason, the possibility of the existence of conformers resulting from internal rotation of some groups is important for understanding the mechanism of corresponding reactions.

2. Experimental

The compounds studied were prepared according to the procedures published earlier [9–11]. The structures were proved by NMR spectroscopy and for compounds **I** and **II** by X-ray single crystal structure analysis. The

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Table 1
 $\nu(\text{CO})$ frequencies (cm^{-1}) for compounds I–V

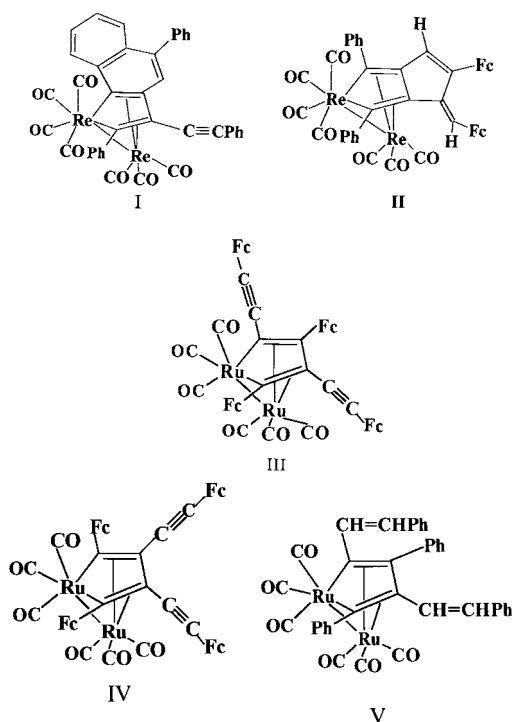
Re complexes			Ru complexes				
I (pentane)	II (CH_2Cl_2)	II (pentane)	III (solid)	III (CH_2Cl_2)	IV (solid)	IV (CH_2Cl_2)	V (solid)
2091m ^a	2087m	2086m	2073s	2076s	2077s	2075s	2077s
2036s	2029s	2034s		2048s	2046s	2048s	2048s
		2029m	2034s		2010s	2007s	2007s
2018m	2014m	2020w	2006s	2011s	1994br	1991s	1992br
		2015s	1987s	1988sh		1970m	
		1994w	1960sh	1970m,br			
1975s	1968s	1978m	1923m				
1970sh		1974s					
1963m	1960s	1965s					
		1955w					
1945m	1930m,br	1941m					
		1933w					

^a s, strong; m, medium; w, weak; br, broad; sh, shoulder.

IR spectra were measured with a Bruker IFS-25 Fourier spectrometer with a resolution of 2 cm^{-1} . The spectra were measured for KBr pellets, CH_2Cl_2 and pentane solutions. Temperature dependent spectra were measured using a Karl Zeiss cryocell with KBr windows. IR spectra in liquefied xenon solution were measured using a specially designed cell. Raman spectra were measured with a Biorad Raman Fourier spectrometer (excitation in the near IR region at 1064 nm by IAG laser). The spectra were processed using a Grams curve-fit program.

3. Results and discussion

IR spectra in the $\nu(\text{CO})$ region were measured for the following complexes I–V (Fc = ferrocenyl):



The $\nu(\text{CO})$ frequencies are presented in Table 1.

In the IR spectrum of compound I in pentane solution (Fig. 1), there are seven carbonyl stretch bands corresponding to seven CO groups in the molecule. Complex II in a CH_2Cl_2 solution has a similar spectrum in the $\nu(\text{CO})$ region, whereas in a pentane solution (Fig. 1) the number of $\nu(\text{CO})$ bands exceeds significantly the number of CO groups. The curve fit procedure has shown the presence of 12 $\nu(\text{CO})$ bands (Fig. 2). With the aim of revealing the temperature behaviour of these bands, the IR spectra of complex II in a pentane solution was measured in the temperature range 300–165 K (Fig. 3). The differential spectra of II, obtained by the subtraction of the spectrum of pentane measured at the same temperature, were treated with the curve fit procedure. The IR spectrum of a pentane solution of II in the $\nu(\text{CO})$ region separated into components is shown in Fig. 2. The relative intensities (the ratio between the absorbances of neighbouring $\nu(\text{CO})$ bands) of the components at various temperatures are presented in Table 2. It can be seen from Table 2 that relative intensities of the four pairs of $\nu(\text{CO})$ bands of complex II change with temperature. These changes are reversible and therefore confirm the existence of a conformational equilibrium between different forms in pentane solution.

In order to examine the dependence of the spectrum in the $\nu(\text{CO})$ region on the solvent nature, the IR spectra in liquefied xenon solution were recorded. The intensity ratio of the bands at 2034 and 2029 cm^{-1} and the bands at 1938 and 1932 cm^{-1} at 165 K differ from those in the spectrum of pentane solution at the same temperature (Fig. 3), that is the intensities of these bands also depend on the solvent nature. Unfortunately, we could only measure the spectra at three temperatures, 190, 215 and 230 K. The spectral pattern

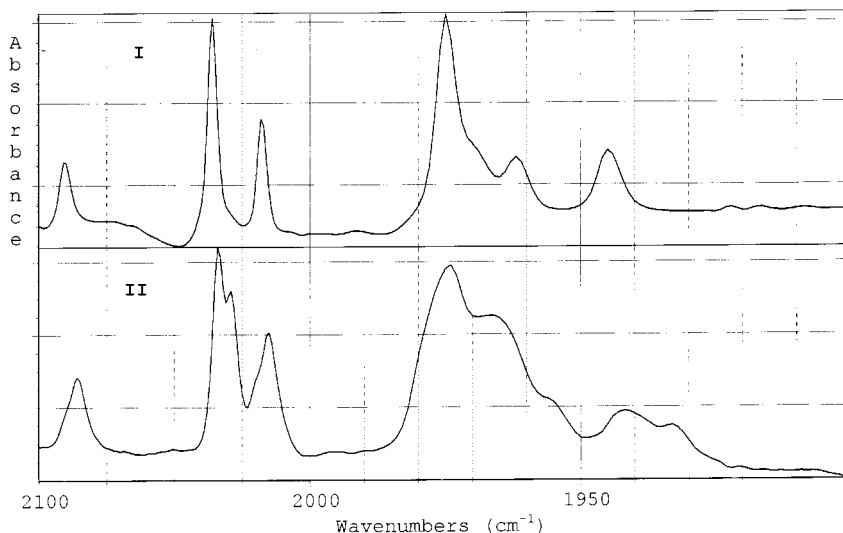


Fig. 1. IR spectra of compounds **I** and **II** in the $\nu(\text{CO})$ region at room temperature in *n*-pentane solutions.

in the $\nu(\text{CO})$ region at these temperatures was processed with the curve fit procedure, which gave ten $\nu(\text{CO})$ bands. The intensity ratio of the bands at 2034/2029 cm^{-1} increased from 0.412 at 190 K to 0.480 at 230 K, the bands at 1976/1974 cm^{-1} increased from 0.958 to 1.122 and the relative intensities of the bands at 1939/1932 cm^{-1} decreased from 0.995 to 0.848 upon heating, i.e. these bands in the xenon solution are also temperature dependent. The solvent and temperature dependence of some $\nu(\text{CO})$ bands in the IR spectra of complex **II** indicate the existence of the equilibrium of two or several forms in solution, which we connect with the internal rotation of the $\text{Re}(\text{CO})_3$ fragment about the multicentered bond of the Re atom with the metallocyclic π -ligand. On heating, the amount of the rotamer with $\nu(\text{CO})$ at 2034, 2020, 1978 and 1933 cm^{-1} increases and at r.t. this rotamer predominates in pentane solution. In xenon solution the composition of the rotamer mixture is, likely, different. The close values of

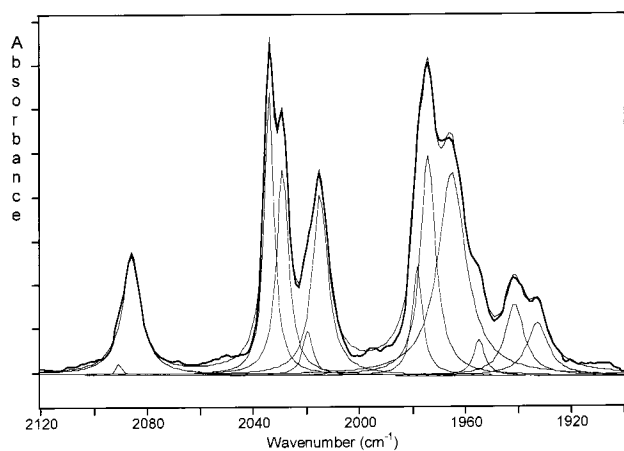


Fig. 2. Contour fit for the IR spectrum of **II** in *n*-pentane solution in the $\nu(\text{CO})$ region.

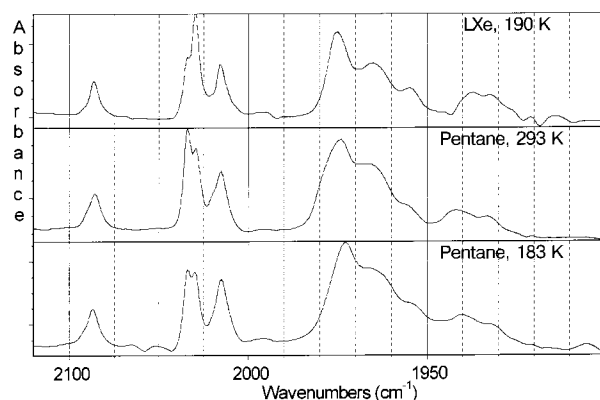


Fig. 3. IR spectra of **II** in pentane solution at 183 and 293 K and liquid xenon solution at 190 K.

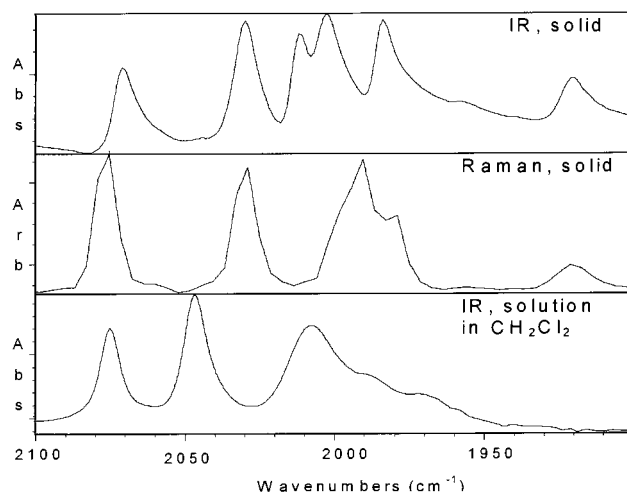


Fig. 4. IR and Raman spectra in the solid state and IR spectrum in CH_2Cl_2 solution of complex **III** in the $\nu(\text{CO})$ region.

Table 2
Relative intensities (A_m/A_n)^a of some $\nu(\text{CO})$ bands at different temperatures for complex **II** in pentane solution

T (K)	$A(2034)/A(2029)$	$A(2020)/A(2015)$	$A(1978)/A(1974)$	$A(1941)/A(1933)$
293	1.359	0.217	0.478	1.383
273	1.366	0.172	0.419	1.646
253	1.435	0.145	0.381	1.870
223	1.477	0.123	0.321	2.176
203	1.456	0.101	0.299	2.213
183	1.001	(0)	0.286	2.067

^a A_m and A_n are the absorbances of corresponding $\nu(\text{CO})$ bands.

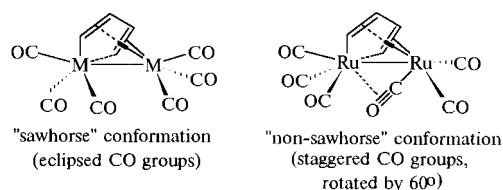
the $\nu(\text{CO})$ frequencies of the rotamers and insignificant temperature changes in the band intensities point to a small energy difference between the rotamers.

A different situation was found for ruthenium complexes **III–V**. In the IR spectrum of compound **III** in the solid (Fig. 4), there are six $\nu(\text{CO})$ bands corresponding to the fragment $\text{Ru}_2(\text{CO})_6$. The Raman spectrum of solid **III** (Fig. 4) contains five $\nu(\text{CO})$ bands and differs from the IR spectrum but both spectra have the low-frequency band at 1920 cm^{-1} . The IR spectrum of a CH_2Cl_2 solution of **III** in the $\nu(\text{CO})$ region (Fig. 4) differs significantly from that of the solid. The band at 1920 cm^{-1} disappears in the spectrum of the solution, but after the evaporation of the solvent the spectral pattern in this region restores. The $\nu(\text{CO})$ bands of complex **IV**, which is a geometrical isomer of **III**, and complex **V** having other substituents are identical in the solid state and in solution and coincide with that of complex **III** in solution, therefore the appearance of the band at 1920 cm^{-1} in the spectrum of the solid cannot result from the crystal effect.

The reversible change in the spectrum of complex **III** on going from the solid to solution gives reason to suppose that **III** has different conformations in the solid state and in solution. In the IR and Raman spectra of solid **III**, one of the $\nu(\text{CO})$ bands has a rather low frequency of 1920 cm^{-1} in comparison to those in the spectra of the analogous complexes **IV** and **V** in solution. This could originate from the fact that one of the CO groups is bound to the adjacent ruthenium atom and can therefore be considered as an asymmetrical bridge (semibridging carbonyl group).

Two conformations have been theoretically predicted by Thorn and Hoffmann [12] for complexes of the ferrole type which result from the rotation of one of the $\text{Fe}(\text{CO})_3$ fragments about the metal–metal bond, namely the ‘sawhorse’ conformation with the eclipsed arrangement of the $\text{Fe}_2(\text{CO})_6$ moiety and the ‘non-sawhorse’ conformation with the staggered arrangement of the $\text{Fe}_2(\text{CO})_6$ moiety, in which one car-

bonyl group forms a weak bond to the adjacent metal atom.



The ‘non-sawhorse’ conformation was found experimentally by X-ray analysis for a number of ferrole type clusters. For example, in $\text{Ru}_2(\text{CO})_6[\text{C}_4(\text{CO}_2\text{Me})_4]$, the ‘non-sawhorse’ conformation with the semibridging carbonyl group was found in the crystal by X-ray analysis [13]. The IR spectrum of this compound, however, was measured only in a hexane solution and has five CO stretching modes, the lowest position being 2021 cm^{-1} [13]. The IR spectrum of this compound in solution does not indicate the presence of the semibridging CO group found in the crystal.

Rotational isomerism, analogous to that found in complex **III**, seems to exist in this complex on going from the solid to solution. Using the IR and X-ray data for a number of Fe clusters, a correlation has been found [14] between the position of the stretch mode of the semibridging carbonyl group and the degree of asymmetry of the bond distances between this carbonyl group and both metal atoms. The highest frequency of 1903 cm^{-1} was reported for the semibridging carbonyl group in $\text{Fe}_3(\text{CO})_8(\text{SC}_4\text{H}_8)_2$, for which the bond length ratio $\text{Fe1-CO}/\text{Fe2-CO} = 1.45$. In the case of **III**, the semibridging CO group has a frequency of 1920 cm^{-1} . If the above correlation is correct, the bonding between the semibridging carbonyl group and the neighbouring ruthenium atom is relatively weak but nevertheless clearly pronounced. This type of conformational isomerism is also associated with the internal rotation about the metal–metal bond, but in this cases these metal atoms are simultaneously involved in π -bonding with organic ligand. Evidently, the ‘non-sawhorse’ conformation with the semibridging carbonyl group is stabilized in the solid by crystal packing. On dissolving this conformation

transforms into the more favourable conformation with terminal CO groups. For complex **III**, we did not find any conformational equilibrium in solution as in the case of complex **II**.

4. Conclusion

Two examples of the novel type of conformational isomerism were found in binuclear rhenium and ruthenium complexes of the ferrole type. Rotamers originate from internal rotation of metal carbonyl groups about the metal–metal bond multisite-bound to the organic ligand. Ruthenium compound **III** exists in the solid state and in solution as two different conformers. In the solid state the ‘non-sawhorse’ conformation with the semibridging carbonyl group was found, which transforms in solution to the conformation containing only the terminal carbonyl groups. Rhenium compound **II** exhibits a conformational equilibrium in solution.

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