

## *trans*-ISOMERS OF TETRACARBONYL HALIDES OF IRON, RUTHENIUM AND OSMIUM

M. PAŃKOWSKI AND M. BIGORGNE\*

Laboratoire de Chimie Minérale, Ecole Nationale Supérieure de Chimie, Paris (France)

(Received July 17th, 1969)

### SUMMARY

Preparation of the compounds *trans*-Fe(CO)<sub>4</sub>I<sub>2</sub> and *trans*-Os(CO)<sub>4</sub>I<sub>2</sub> is described and vibrational assignment based on their infrared spectra are discussed from a structural viewpoint. *trans*-Ru(CO)<sub>4</sub>I<sub>2</sub> could not be isolated in a pure state. All these compounds exist in the *cis* and *trans* forms in the solid state as well as in solution. Dependence of the equilibrium upon radiation and temperature is also discussed.

### INTRODUCTION

*Cis-trans* isomerism of M(CO)<sub>4</sub>X<sub>2</sub> (M = Fe, Ru, Os; X = I, Br, Cl) offers an interesting subject for investigation in spectroscopy. These compounds are monomers of octahedral configuration and are known in literature as having the *cis* form<sup>1-3</sup>: the two metal-halogen bonds form an angle of 90°. This configuration corresponding to the point group C<sub>2v</sub>, should show four C-O infrared active bands (2A<sub>1</sub> + B<sub>1</sub> + B<sub>2</sub>), four M-C bands (2A<sub>1</sub> + B<sub>1</sub> + B<sub>2</sub>), two M-X (A<sub>1</sub> + B<sub>1</sub>) and six M-C-O bands (2A<sub>1</sub> + 2B<sub>1</sub> + 2B<sub>2</sub>).

On the contrary, for the *trans* isomers of these compounds, one should expect, in the case of the highest molecular symmetry D<sub>4h</sub>: one C-O band E<sub>u</sub>, one M-C band E<sub>u</sub>, one M-X band A<sub>2u</sub> and two M-C-O bands A<sub>2u</sub> + E<sub>u</sub>.

IR analysis should therefore enable to distinguish between these two isomers without ambiguity.

### RESULTS AND DISCUSSION

#### *Synthesis of trans-M(CO)<sub>4</sub>I<sub>2</sub> complexes*

Detection of the *trans* form has been realized for the first time by Noack<sup>1</sup> for Fe(CO)<sub>4</sub>I<sub>2</sub>: when a solution of *cis*-Fe(CO)<sub>4</sub>I<sub>2</sub> in hexane was exposed to the spectrograph beam, a new band appeared at 2081.0 cm<sup>-1</sup>, which was supposed to belong to the *trans* complex. This phenomenon was observed also by Johnson *et al.*<sup>4</sup> who studied combination bands in the region 4300-4100 cm<sup>-1</sup> of a *cis/trans* mixture.

\* Author to whom correspondence should be addressed.

Using Noack's method we succeeded in isolating<sup>5</sup> *trans*-Fe(CO)<sub>4</sub>I<sub>2</sub> in the pure state. A solution of the *cis* form in hexane exposed to sunlight was converted in a 30% yield into the *trans* form, with other decomposition byproducts.

The mixture was separated by fractional crystallisation at -80°, the *trans* form being less soluble than the *cis*. The *cis/trans* solid mixture may be also fractionated by sublimation at room temperature under a current of nitrogen gas, the *trans* form being more volatile than the *cis* one. The *trans* form can also be obtained, besides the action of light, by heating the *cis* form in an autoclave for 48 h under a CO pressure of 300 atm at 135°, but the conversion ratio is very weak.

Os(CO)<sub>4</sub>I<sub>2</sub> was synthesised for the first time by Hieber and Stallmann<sup>10</sup> by the action of CO on "Osmiumoxyiodide" under a CO pressure of 200 atm at various temperatures. These authors observed the formation of two types of crystals according to the reaction temperature. Hales and Irving<sup>3</sup> obtained *cis*-Os(CO)<sub>4</sub>I<sub>2</sub> by employing the same method (temperature not indicated).

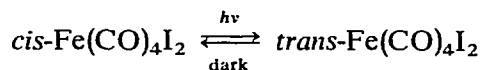
Attempts to modify Hieber's method led us to heat only the lower part of the autoclave containing "Osmiumoxyiodide" up to 60° during 24 h under a CO pressure of 300 atm. On the upper (colder) part of the autoclave yellowish crystals were formed: these were found to have the formula OsC<sub>4</sub>O<sub>4</sub>I<sub>2</sub> and their *trans* structure was confirmed by IR analysis (Fig. 2). (Found: C, 8.78. C<sub>4</sub>I<sub>2</sub>O<sub>4</sub>Os calcd.: C, 8.65%.)

*Trans* complexes could not be obtained by the action of sunlight on hexane solutions of *cis*-Os(CO)<sub>4</sub>I<sub>2</sub>. Solutions of *cis*-Ru(CO)<sub>4</sub>I<sub>2</sub> in hexane when exposed to sunlight, give reaction products whose IR spectra show a number of new bands out of which the one at 2089.5 cm<sup>-1</sup> may be assignable to the expected *E* band of the *trans* form<sup>7-9</sup>. This band is close to the B<sub>2</sub> axial band at 2106.0 cm<sup>-1</sup>, the strongest band in the spectrum of the *cis* form; the same phenomenon is observed with iron complex isomers. This assignment may be confirmed by studying the modifications of the *cis*-Ru(CO)<sub>4</sub>I<sub>2</sub> spectrum when this compound is heated during 48 h at 170° under a CO pressure of 300 atm.

Several experiments showed that only one new band appears in the spectrum at 2089.5 cm<sup>-1</sup>, variable in intensity from one experiment to another and from one sample to another of the same preparation.

#### *cis-trans* Equilibrium

Contrary to reports by Johnson *et al.*<sup>4</sup> our observations show that the *cis-trans* rearrangement results from the equilibrium:



in the following manner:

- Exposure to light of the *cis* form results in a partial transformation to the *trans* form with simultaneous decomposition.
- By keeping a solution of the *trans* form in darkness at room temperature, formation of the *cis* form follows.

These observations confirm the existence of an equilibrium which is displaced in favor of the *cis* form, in the absence of light and at room temperature.

*cis*-Ru(CO)<sub>4</sub>I<sub>2</sub> behaves in the same manner under the action of sunlight as *cis*-Fe(CO)<sub>4</sub>I<sub>2</sub>; however the reaction gives in addition to the *trans* form some other

carbonyl complexes. As for the *cis*-Os(CO)<sub>4</sub>I<sub>2</sub> complex, it decomposes when exposed to sunlight without giving the *trans* form, while *trans*-Os(CO)<sub>4</sub>I<sub>2</sub> is converted into the *cis* form under the same conditions.

Solid *cis*-Fe(CO)<sub>4</sub>I<sub>2</sub> when heated to 135° under 300 atm of CO partially transforms to the *trans* form. *cis*-Ru(CO)<sub>4</sub>I<sub>2</sub> seems to have a similar behaviour at 170° and the same conditions of pressure.

In the case of the *trans*-Os(CO)<sub>4</sub>I<sub>2</sub> the behaviour seems to be inverted: the transformation of the *cis* form was nearly total at 200° and 300 atm of CO (the *trans* form was obtained at 60°).

Our investigations indicate that the reaction equilibrium under the conditions which we have described (CO pressure) is displaced in favor of the *cis* form for iron and ruthenium complexes and in favor of the *trans* form in the case of the osmium complexes, at room temperature.

*Spectroscopic study*

In a separate paper<sup>6</sup> it is shown that the appearance of the *B*<sub>1g</sub> band in the spectra of *trans*-Fe(CO)<sub>4</sub>I<sub>2</sub> and in *trans*-Os(CO)<sub>4</sub>I<sub>2</sub> is due to lowering of the molecular symmetry.

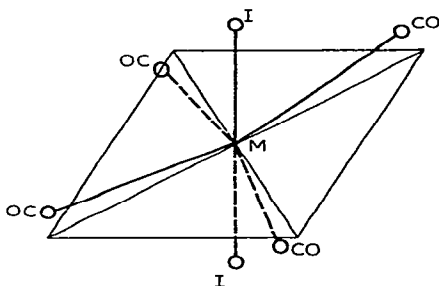


Fig. 1. Configuration of *trans*-M(CO)<sub>4</sub>I<sub>2</sub> complexes (*D*<sub>2d</sub>).

The molecular symmetry is actually *D*<sub>2d</sub> and not *D*<sub>4h</sub>.

The number and species of the expected bands of both *D*<sub>4h</sub> and *D*<sub>2d</sub> point group symmetry are summarised in Table 1.

TABLE 1

NUMBER AND SPECIES OF EXPECTED C-O, M-C, M-C-O AND M-X BANDS FOR *trans*-M(CO)<sub>4</sub>I<sub>2</sub> COMPLEXES

C-O stretching		M-C-O bending		M-X stretching	
M-C stretching					
<i>D</i> <sub>4h</sub>	<i>D</i> <sub>2d</sub>	<i>D</i> <sub>4h</sub>	<i>D</i> <sub>2d</sub>	<i>D</i> <sub>4h</sub>	<i>D</i> <sub>2d</sub>
<i>A</i> <sub>1g</sub>	<i>A</i> <sub>1</sub>	<i>A</i> <sub>2g</sub>	<i>A</i> <sub>2</sub>	<i>A</i> <sub>1g</sub>	<i>A</i> <sub>1</sub>
<i>B</i> <sub>1g</sub>	<i>B</i> <sub>2<sup>a</sup></sub>	<i>B</i> <sub>2g</sub>	<i>B</i> <sub>1</sub>	<i>A</i> <sub>2u<sup>a</sup></sub>	<i>B</i> <sub>2<sup>a</sup></sub>
<i>E</i> <sub>u<sup>a</sup></sub>	<i>E</i> <sup>a</sup>	<i>E</i> <sub>g</sub>	<i>E</i> <sup>a</sup>		
		<i>A</i> <sub>2u<sup>a</sup></sub>	<i>B</i> <sub>2<sup>a</sup></sub>		
		<i>B</i> <sub>2u</sub>	<i>A</i> <sub>1</sub>		
		<i>E</i> <sub>u<sup>a</sup></sub>	<i>E</i> <sup>a</sup>		

<sup>a</sup> IR-active.

The modifications concern three bands: two bands of  $B_2$  symmetry (C–O and M–C) and one of  $E$  symmetry M–C–O for  $D_{2d}$ . One expects that these bands should be of very weak intensity owing to the fact that the  $D_{2d}$  configuration of the molecule results from a distortion of  $D_{4h}$  symmetry.

CO bands of  $B_2$  species were observed without any ambiguity in the pure *trans*- $\text{Fe}(\text{CO})_4\text{I}_2$  and *trans*- $\text{Os}(\text{CO})_4\text{I}_2$  in solution. They are more intense in iron than in osmium complexes. A possible repulsion of the CO's between them has been suggested<sup>6</sup> as the cause of the lowering of the symmetry from  $D_{4h}$  to  $D_{2d}$ . The weaker intensity of the  $B_2$  band in the osmium complex would follow from the bigger size of this atom: the distance between the CO's is larger, and their repulsion smaller.

We did not succeed in isolating *trans*- $\text{Ru}(\text{CO})_4\text{I}_2$  without contamination with *cis* isomer, in order to locate the corresponding  $B_2$  band.

$E$  (M–C–O) bands corresponding to  $E_g$  species of  $D_{4h}$  were not detected even in the case of iron and osmium complexes. It is possible that they have the same frequencies as the  $E$  bands corresponding to  $E_u$  species of  $D_{4h}$  symmetry. Finally the  $B_2$  axial (M–C) bands of *trans* iron and osmium complexes were not distinguished with full certainty.

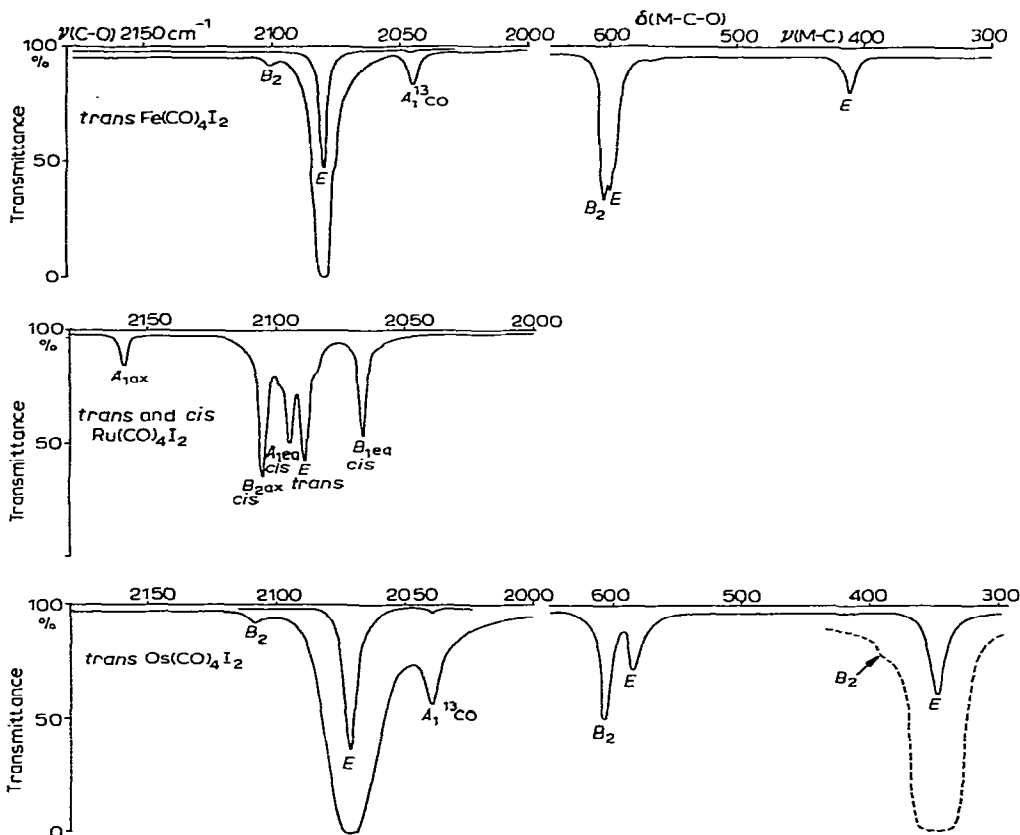


Fig. 2. IR spectra of *trans*- $\text{M}(\text{CO})_4\text{I}_2$  ( $\text{M} = \text{Fe}, \text{Os}$ ) and *cis/trans*  $\text{Ru}(\text{CO})_4\text{I}_2$  mixture in the C–O and M–C stretching region and in the M–C–O bending region in hexane solutions (dotted curve of *trans*- $\text{Os}(\text{CO})_4\text{I}_2$  in Os–C region in CsI pellet).

Fig. 2 represents the spectra of the pure *trans*-Fe(CO)<sub>4</sub>I<sub>2</sub> and *trans*-Os(CO)<sub>4</sub>I<sub>2</sub> and a *cis/trans* Ru(CO)<sub>4</sub>I<sub>2</sub> mixture.

The assignments are evident for *E* (C–O) and (M–C) bands. The *B*<sub>2</sub> (C–O) band was previously<sup>5</sup> designated *B*<sub>1g</sub>. Weak bands situated at the lower frequency side of *E* (C–O) bands are undoubtedly related to *trans*-M(<sup>13</sup>CO)(<sup>12</sup>CO)<sub>3</sub>I<sub>2</sub> species vibrations.

In the region of M–C–O bending, the band of higher frequency is assigned to the *B*<sub>2</sub> vibration by comparison with homologous *trans*-Fe(CO)<sub>3</sub>[P(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>. If this is so, the second band would then be of the *E* species.

The frequencies of the M–C–O and M–C vibrations of *cis*-ruthenium and *cis*-osmium complexes are given in Table 2 for the first time.

TABLE 2

ABSORPTION BANDS<sup>a</sup> AND ASSIGNMENTS OF C–O, M–C–O AND M–C VIBRATIONS OF *cis* AND *trans*-M(CO)<sub>4</sub>I<sub>2</sub> COMPLEXES (M = Fe, Ru, Os)

Fe(CO) <sub>4</sub> I <sub>2</sub>		Ru(CO) <sub>4</sub> I <sub>2</sub>		Os(CO) <sub>4</sub> I <sub>2</sub>	
<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>
C <sub>2v</sub>	D <sub>2d</sub>	C <sub>2v</sub>	(D <sub>2d</sub> )	C <sub>2v</sub>	D <sub>2d</sub>
C–O					
2131.0 s A <sub>1ax</sub>	2102.0 vw B <sub>2</sub>	2159.5 m A <sub>1ax</sub>		2163 m A <sub>1ax</sub>	2108 vw B <sub>2</sub>
2086.7 vs B <sub>2ax</sub>	2081 vs E	2106.0 s B <sub>2ax</sub>	2089.5 vs E	2099.5 s B <sub>2ax</sub>	2073.0 vs E
2084.9 (sh) A <sub>1eq</sub>		2095.0 s A <sub>1eq</sub>		2084.5 s A <sub>1eq</sub>	
2062.0 s B <sub>1eq</sub>	2047 vw A <sub>1</sub> ( <sup>13</sup> CO)	2067.0 s B <sub>1eq</sub>		2049.5 s B <sub>1eq</sub>	2040 vw A <sub>1</sub> ( <sup>13</sup> CO)
M–C–O					
600 vs	606 vs B <sub>2</sub>	559 vs <sup>b</sup>		573 vs <sup>b</sup>	606.5 vs B <sub>2</sub>
594 vs	600 vs E	549 vs <sup>b</sup>		563 vs <sup>b</sup>	585 s E
573 vs		538 vs <sup>b</sup>		552 vs <sup>b</sup>	
507 w				535 (sh) <sup>b</sup>	
				531 (sh) <sup>b</sup>	
M–C					
454 m		458 m <sup>b</sup>		463 m <sup>b</sup>	
421 w		432 w <sup>b</sup>		439 w <sup>b</sup>	
395 vw		385 m <sup>b</sup>		403.5 m <sup>b</sup>	380 <sup>b</sup> (sh) B <sub>2</sub>
385 m		339 s B <sub>2ax</sub> <sup>b</sup>		350 s B <sub>2ax</sub> <sup>b</sup>	347 s E

<sup>a</sup> All spectra (solutions in hexane unless stated otherwise) recorded using a Perkin–Elmer 225 spectrophotometer; vw, very weak; w, weak; m, medium; s, strong; vs, very strong; (sh), shoulder. <sup>b</sup> In CsI pellet.

In view of their high intensities the bands at 339 cm<sup>-1</sup> of *cis*-Ru(CO)<sub>4</sub>I<sub>2</sub> and 350 cm<sup>-1</sup> of *cis*-Os(CO)<sub>4</sub>I<sub>2</sub> are assigned to *B*<sub>2</sub> axial species vibrations (two M–C bonds *trans* to each other).

In conclusion it can generally be stated that the ruthenium complexes are not situated between those of iron and osmium, as far as their frequencies are concerned. This behaviour is closely related to that of the homologous series of chromium, molybdenum and tungsten hexacarbonyls.

## REFERENCES

- 1 K. NOACK, *Helv. Chim. Acta*, 45 (1962) 1847.
- 2 E. R. COREY, M. V. EVANS AND L. F. DAHL, *J. Inorg. Nucl. Chem.*, 24 (1962) 926.
- 3 L. A. W. HALES AND R. J. IRVING, *J. Chem. Soc., A*, (1967) 1389.
- 4 B. F. G. JOHNSON, L. LEWIS, P. W. ROBINSON AND R. MILLER, *J. Chem. Soc., A*, (1968) 1043.
- 5 M. PAŃKOWSKI AND M. BIGORGNE, *C. R. Acad. Sci., Paris*, 263 (1966) 239.
- 6 M. BIGORGNE, R. POILBLANC AND M. PAŃKOWSKI, *Spectrochim. Acta*, in press.
- 7 F. CALDERAZZO, *Halogen Chemistry*, Vol. 3, Academic Press, New York, 1967, p. 411.
- 8 F. CALDERAZZO AND F. L. EPLATTENIER, *Inorg. Chem.*, 6 (1967) 1220.
- 9 B. F. G. JOHNSON, R. D. JOHNSTON AND J. LEWIS, *J. Chem. Soc., A*, (1969) 792.
- 10 W. HIEBER AND H. STALLMANN, *Chem. Ber.*, 75 (1942) 1472.

*J. Organometal. Chem.*, 19 (1969) 393-398