Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

METAL-LIGAND VIBRATION FREQUENCIES IN π- AND σ-INDENYL- AND CYCLOPENTADIENYL-METAL COMPLEXES

EDMOND SAMUEL AND MICHAËL BIGORGNE
Laboratoire de chimie de coordination, 11 rue P. et M. Curie, Paris Ve (France)

(Received February 16th, 1971)

SUMMARY

The Raman and infrared spectra of π-indenyl complexes of Fe and Ru and of σ-indenyl complexes of Hg have been examined in the low-frequency region, and a tentative assignment of the metal-to-ring and metal-to-carbon symmetrical stretching frequencies made. These are compared with the frequencies in the homologous cyclopentadienyl compounds, and the observed shifts in frequencies are discussed.

While the infrared and Raman spectra of many π- and σ-bonded cyclopentadienyl–metal compounds have been extensively studied[1], spectral data on indenyl–metal compounds remain scanty. In most cases, the infrared spectra or frequencies have been given without assignments[2-4], and no low-frequency infrared or Raman measurements have to our knowledge been mentioned. The lower symmetry of the indenyl group (C_9H_7), and the higher number of vibrators when compared to its cyclopentadienyl homologue (C_5H_5), renders the complete vibrational assignment, even of molecules with simple structures, such as Ind_2Fe and Ind_2Ru*, a complex undertaking.

In Raman spectra, totally symmetric fundamentals can in some cases be easily identified because of their strong intensity and polarization. In the low-frequency region (600 to 50 cm^{-1}) these can arise either from symmetrical metal-ring stretching modes in the π-complexes and metal–carbon stretch in the σ-complexes, or from inner deformations of the ring. Through comparative studies, we have been able to assign skeletal stretching modes in some π- and σ-compounds.

In this work, we report infrared and Raman measurements undertaken on the π-indenyl complexes Ind_2Fe and Ind_2Ru, and on the σ-complexes IndHgX ($X = Cl$, Br and Ind), with a view to determining mainly their skeletal vibrations and comparing these with results already known for their cyclopentadienyl homologues.

EXPERIMENTAL

Complexes

All the complexes studied were prepared according to methods already described.

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* In this work Ind and Cp depict indenyl (C_9H_7) and cyclopentadienyl (C_5H_5) groups.

Di-π-indenyliron. Ind_2Fe was prepared from the reaction of indenylsodium in THF on a suspension of $FeCl_2$ in the same solvent, followed by solvent evaporation and extraction of the residue with benzene[2-4].

Di-π-indenylruthenium. Ind_2Ru was prepared by a similar procedure which was slightly modified, the THF solution of indenylsodium being slowly added with stirring to a solution of $RuCl_3$ in THF (ratio 3/1 moles). When the addition was over, the suspension was refluxed for 2 h, the solvent removed and the solid residue sublimed under vacuum to give light-orange crystals (yield about 18%).

π-Indenylmercury chloride. IndHgCl was prepared from indenylsodium and $HgCl_2$ in THF[5] at −80°.

Di-σ-indenylmercury. Ind_2Hg was prepared using an improved form of a procedure described previously[5]. Thus, a suspension of IndHgCl in dichloroethylene was shaken in a separatory funnel with an aqueous solution of KI, and after decantation the organic layer was dried over $CaCl_2$. Some of the solvent was then removed under vacuum and the remainder left for a few hours at −30°, when light-yellow crystals of Ind_2Hg begin separating.

Raman spectra

These were measured using a Coderg spectrophotometer with a laser source, and with dry THF as a solvent. THF has only a few weak bands in the spectra region 800 to 0 cm^{-1}.

RESULTS

π-Indenyl complexes of Fe and Ru

From crystallographic measurements it has been established that Ind_2Ru has a fully eclipsed configuration while Ind_2Fe shows a staggered configuration[7], as shown in Fig. 1, so that the first compound should have C_{2v} symmetry while the second should possess C_1 symmetry in the solid state. However, with the exception of the A_2 bands which are infrared forbidden in the C_{2v} symmetry group, the same number of bands should be active in the Raman and infrared spectra for both complexes. Almost identical spectra for both compounds should also be expected as far as the inner vibrations of the indenyl ligand are concerned.

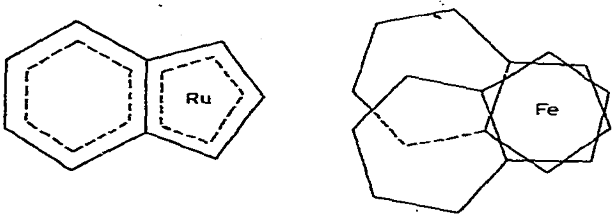

Fig. 1. Molecular configurations of Ind_2Fe and Ind_2Ru.

The observed spectra are indeed identical in the spectral region 3000 to 600 cm^{-1} where mainly such vibrations are expected to occur, and they differ only in the skeletal vibrations region (400 to 50 cm^{-1}). The main important features of the infrared spectra are:

(*a*). Absence in the Ind_2Fe spectrum of the strong band at 1100 cm^{-1} which is present in ferrocene, indicating substitution in both of the C_5 rings of the latter compound.
(*b*). Presence of a sharp intense band at 1000 cm^{-1} due to symmetric ring breathing. This band appears at 1015 cm^{-1} in the spectrum of ferrocene and is also of strong intensity[8].
(*c*). Presence also of a sharp intense band at 800 cm^{-1} which is probably of the same origin as the 804 cm^{-1} band in the spectrum of ferrocene [ω(CH) bending of the C_5 ring[8]].
(*d*). The sharp doublet at 750 cm^{-1} is due to the *ortho*-substituted phenyl ring.
(*e*). The strong doublet at 478 and 490 cm^{-1} in the ferrocene spectrum (antisymmetric ring–metal–ring stretch and symmetric ring tilt respectively[8]) is absent in this case. On the other hand, two bands of medium intensity lying at 560 and 465 cm^{-1} are observed. They occur at exactly the same frequencies in both Ind_2Fe and Ind_2Ru (Fig. 2).

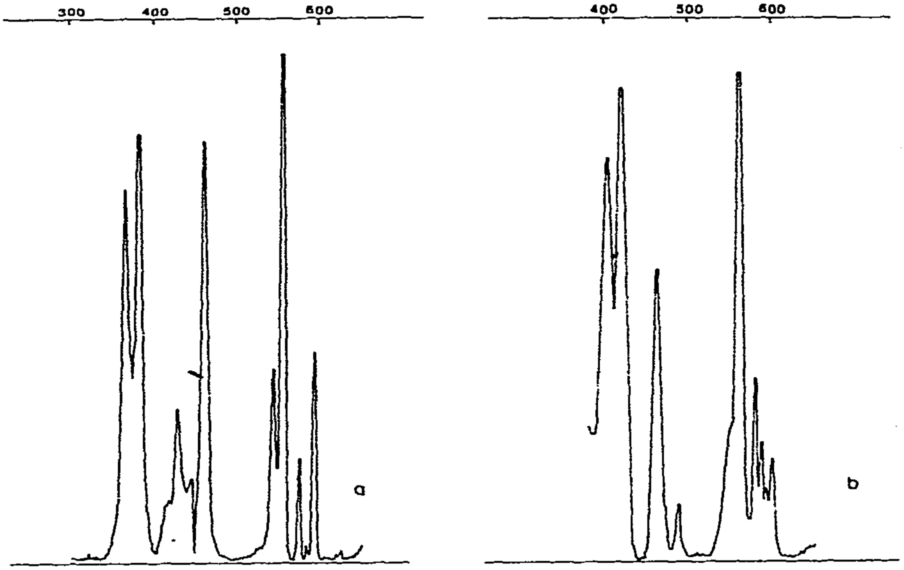

Fig. 2. Infrared spectra of (a) Ind_2Fe and (b) Ind_2Ru in the region 300 to 600 cm^{-1} (in nujol).

Low-frequency region (*infrared*). Starting from 300 cm^{-1} down to low frequencies, five major bands having the same relative intensities are observed in the spectra of Ind_2Fe and Ind_2Ru (Fig. 3). They lie at the following frequencies:

Ind_2Fe	288, 250, 225, 148 and 127 cm^{-1}
Ind_2Ru	300, 234, 204, 148 and 132 cm^{-1}

This similarity in features suggests that, as expected, the deviation from C_{2v} symmetry in Ind_2Fe does not affect its vibrational modes when compared to Ind_2Ru. Both compounds also show an increased number of bands when compared to ferrocene or to ruthenocene. In view of the complexity of these spectra, it is difficult to give assignments to all the bands observed, but some important modes may be correlated

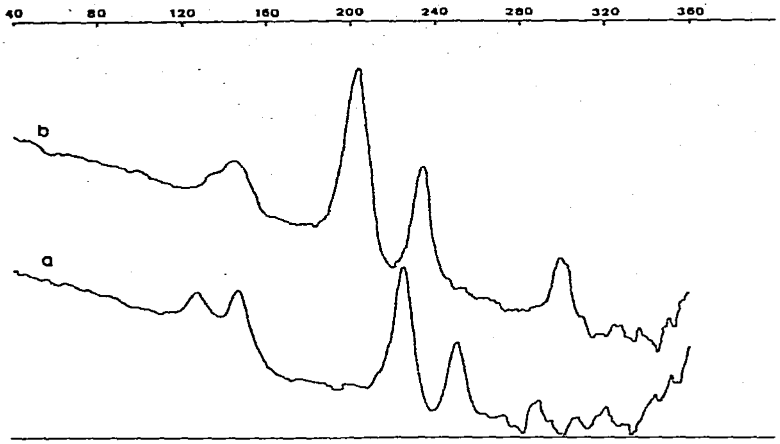

Fig. 3. Infrared spectra of (a) Ind_2Fe and (b) Ind_2Ru in the region 40 to 360 cm^{-1} (in polyethylene).

tentatively on the basis of the Raman spectra, all bands of which should also be infrared active.

Raman spectra. These could be obtained only in the case of Ind_2Ru, the deep purple colour of the Fe compound being unfavourable to this type of spectral investigation. In the low-frequency region (700 to 50 cm^{-1}), one intense polarized band lying at 310 cm^{-1} is predominant, the other being of low intensity. This band may be attributed to the symmetric metal–ring stretching vibration on the basis of assignments made previously for similar sandwich compounds from Raman evidence[8] (Cp_2Fe and Cp_2Ru for instance, also show strong polarized bands at 306 and 330 cm^{-1} respectively, both being infrared forbidden in point groups D_{5h} and D_{5d}). The infrared counter part should then be the band of weak intensity lying at 300 cm^{-1}, to which a band lying at 288 cm^{-1} (of similarly weak intensity) corresponds in the Fe compound. This latter band may therefore be identified as the symmetric metal-ring stretch in Ind_2Fe.

For the antisymmetric metal–ring stretching modes, the corresponding bands should also be both infrared and Raman active and may be expected to lie at higher frequencies than those for the symmetric stretching modes (negative interaction force constant), as is usually observed in organometallic compounds. The most likely candidates for these modes are the IR bands (Fig. 2) of medium intensity lying at:

550, 500 and 420, 404 cm^{-1} in Ind_2Fe

550, 500 and 360, 380 cm^{-1} in Ind_2Ru

The first two bands may be ruled out since they lie at exactly the same frequencies in both compounds. Thus, the second sets of bands, seem to be the only suitable ones which may be attributed to this mode. This assignment places the antisymmetric mode for the Ru compound at a lower frequency than that for the Fe compound, as is the case with the cyclopentadienyl derivatives. Table 1 shows the comparative values of symmetric and antisymmetric metal–ring stretching frequencies in R_2M compounds (R = Cp, Ind and M = Fe, Ru).

It follows from the above assignments that the ν_{sym} (M–ring) in the indenyl compounds of Fe and Ru lie at lower frequencies than in the cyclopentadienyl homo-

TABLE 1

COMPARATIVE VALUES OF SYMMETRIC AND ANTISYMMETRIC METAL–RING STRETCHING FREQUENCIES IN R_2M COMPOUNDS (R = Cp, Ind; M = Fe, Ru)

Compound	Symm. M–ring stretch (cm^{-1})	Antisym. M–ring stretch (cm^{-1})
Cp_2Fe	306	478 (ref. 8)
Cp_2Ru	330	446 (ref. 8)
Ind_2Fe	288	404 or 420 (this work)
Ind_2Ru	310	366 or 380 (this work)

TABLE 2

COMPARATIVE VALUES OF SYMMETRIC METAL–RING STRETCHING FREQUENCIES IN R_2Fe, $RMn(CO)_3$, $R'Cr(CO)_3$ COMPOUNDS AND THEIR METHYL HOMOLOGUES (R = Cp; R' = C_6H_6)

Compound	
Cp_2Fe	306 (ref. 8)
$(MeC_5H_4)_2Fe$	311 (ref. 9)
$CpMn(CO)_3$	354
$(MeC_5H_4)Mn(CO)_3$	361
$C_6H_6Cr(CO)_3$	298 (ref. 10)
$1,3,5\text{-}Me_3C_6H_3Cr(CO)_3$	329 (ref. 11)

logues. This shift may be attributed to a lower M–ring force constant and consequently, to a weaker bonding due to the electron-withdrawing character of the phenyl substituent fused to the C_5 ring.

This argument is supported by measurements undertaken on bis(tetrahydroindenyl)ruthenium[3], whose Raman spectrum exhibits a strong polarized band lying at 360 cm^{-1}, which may be assigned to the symmetric metal–C_5-ring stretch. Another polarized band of medium intensity was present at 250 cm^{-1}, but its origin could not be explained. This indicates that by saturation, the phenyl ring is transformed into an electron releasing substituent which increases the metal–ring force constant and strengthens the binding between the metal and the ring. The following data in Table 2 gathered from the literature tend to confirm this assumption.

σ-complexes of mercury

Sufficient evidence has been put forward to confirm that in compounds such as IndHgX (X = Cl, Br, Ind) and their cyclopentadienyl homologues, the metal is bonded to the sp^3 carbon of the C_5 ring, and not by a delocalized bond to the entire ring[5,12,13]. It was of interest to determine the ν(Hg–C) stretch in the σ-indenyl derivatives in order to compare this with the corresponding frequency in the cyclopentadienyl homologues, as well as with other organomercury compounds such as RHgX (X = halogen, R and R = alkyl).

Symmetric Hg–C stretching frequencies occur at about 550 cm^{-1} in alkylmercury compounds[14,15], and they usually give rise to intense bands in the Raman spectrum. It may be expected therefore, that indenyl derivatives of mercury would also show a band corresponding to a Hg–C stretch at this frequency or lower. Examination of the Raman spectra of the IndHgX compounds (in THF) in the region 700 to 50 cm^{-1} showed several common features (Table 3). Three or four polarized bands of medium

TABLE 3

RAMAN SPECTRA (0 TO 700 cm^{-1}) OF RHgX AND R_2Hg COMPOUNDS (R = Cp, Ind; X = Cl, Br)

IndHgCl	CpHgCl	IndHgBr	CpHgBr	Ind_2Hg	Cp_2Hg	Assignments
207 w,d	200 w	202 vs,p	212 m	175 s,p	158 w,d	C–Hg–C bend
	187 w			198 s,p	185 vs,p	
330 s,p	315 vs,p	240 s,p	230 s,p			ν(Hg–X)
380 w	355 w	380 s,p	348 m	370 vs,p	345 s,p	ν(Hg–C)
430 w,d		435 w,d		435 w,d	448 w	
665 m,p	658 m	662 s,p	658 m	662 s,p	655 s,p	C–H deform.

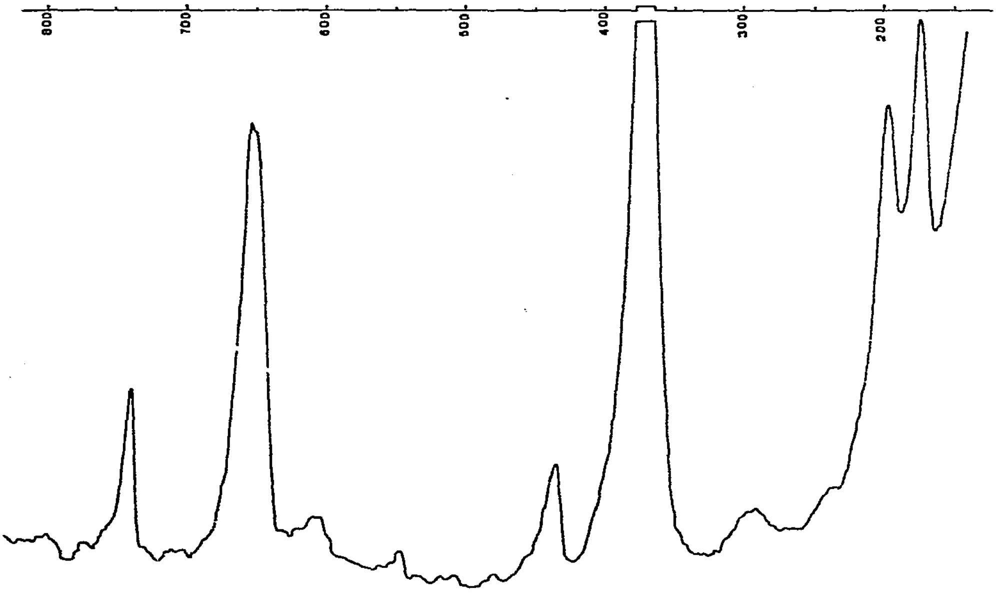

Fig. 4. Raman spectra of Ind_2Hg and Cp_2Hg in THF solution.

and strong intensity were observed, (Fig. 4). The band at 660 cm^{-1}, absent in the spectra of the π-indenyl complexes, is related to the C–H bending modes of the C_5 ring, and its intensity is appreciably reduced upon partial deuteration of this ring. The bands due to ν(Hg–X) (X = Cl, Br) could be identified without difficulty, but the two bands lying at 175 and 198 cm^{-1} could not be assigned with any certainty; their low frequency precludes any possibility of assigning them to the Hg–C stretching mode. One of them, however, might be related to C–Hg–C bending modes, on the basis of similar observations made on phenyl- and alkylmercury compounds[16,17].

One band in the spectrum, lying at 370 cm^{-1}, remains to be identified. It is polarized, of strong intensity in Ind_2Hg, becomes weaker in the bromide, and dwindles considerably in the chloride. We have assigned it to the symmetric Hg–C stretching mode for the following reasons:

(*a*). It is the only band sensitive towards the nature of the substituent X.

(*b*). It lies at a frequency which may be reasonably expected for a metal–carbon stretch.

(*c*). It is absent in the spectrum of indene itself and in those of the indenyl π-complexes examined.

The spectra of the homologous cyclopentadienyl derivatives exhibited identical features as far as the number of bands present and their respective intensities are concerned. According to previous assignments made by Maslowsky and Nakamoto[13], the symmetric ν(Hg–C) lies in Cp_2Hg at 321 cm^{-1} from the basis of its Raman spectrum in CCl_4 solution. According to our measurements, an intense polarized band may be observed at 345 cm^{-1} (the band at 321 cm^{-1} was absent) which became weaker in the spectrum of the bromide and even weaker in that of the chloride. This band therefore follows the same behavior as the band present at 370 cm^{-1} in the spectra of the indenyl compounds, and hence may be attributed to ν(Hg–C) in the cyclopentadienyl compounds. Both of these bands relate to corresponding infrared-active bands of medium intensity.

CONCLUSION

From the above study it follows that:

(*a*). the metal–ring symmetrical stretching frequency in the π-compounds depends mainly on the electron density of the ring and not on its reduced mass; the following trend was observed in the compounds studied:

$(H_4Ind)_2Ru > Cp_2Ru > Ind_2Ru$

(*b*). the Hg–C stretch in the indenyl–mercury compounds lies at a higher frequency than in the cyclopentadienyl homologues

ν(Hg–C) in $Ind_2Hg > Cp_2Hg$

This is the reverse trend to that observed in the case of the π-complexes and could be explained by an enhanced electron density at the C_1 atom of the indenyl ring compared to that in the cyclopentadienyl ring. However, additional measurements on similar σ-bonded compounds are needed to lend support to this argument.

(*c*). The metal–ring stretching frequency in the π-complexes is of the same order of magnitude as the metal–carbon stretching frequency in the σ-complexes (both lie between 300 and 400 cm^{-1}). This does not signify, however, that the relative force constants are comparable to each other.

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