

CHARACTERISATION BY INFRARED OF π - AND σ -BONDING IN METAL-INDENYL COMPLEXES: A STUDY OF MERCURY, TIN AND PALLADIUM DERIVATIVES

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SUMMARY

Synthesis of the new indenyl compound, Ind_2Hg as well as IndHgX ($X = \text{Cl}, \text{Br}$), is described. Although their structure could not yet be elucidated from NMR measurements, a comparison of their IR spectra with those of π -indenyl complexes shows that in the C-H stretching and deformation regions, the presence of some characteristic bands indicates a σ -metal-to-carbon bonding.

Another new indenyl compound (IndPdCl)₂ is also described. Preliminary IR and NMR measurements do not allow the nature of palladium-indenyl bonding to be determined with certainty.

INTRODUCTION

Various recent studies have led us to consider some cyclopentadienyl compounds, like $\pi\text{-CpFe}(\text{CO})_2\text{-}\sigma\text{-Cp}$, $\pi\text{-CpCr}(\text{NO})_2\text{-}\sigma\text{-Cp}$ and $\sigma\text{-CpCuEt}_3\text{P}$, as belonging to a separate class in which the σ -bonded ring exhibits fluxional behaviour¹; a satisfactory explanation of their anomalous NMR spectra has thus been provided. However, the true nature of metal-to-ring bonding (π or σ) in some cyclopentadienyl complexes of nontransition elements (Cp_2Hg , CpHgCl , Cp_4Sn , Cp_4Pb) is still subject to speculation²⁻⁴. No unequivocal answer has been brought forward as yet by NMR measurements.

Since transition metal-indenyl complexes⁵⁻⁸ show a remarkable similarity in structure to their cyclopentadienyl homologues, we thought that a study of indenyl complexes with nontransition metals would shed more light on this interesting subject. The lowering of the number of protons of the metal-bonded ring from 5 to 3 would be expected to make the IR and NMR spectra show more distinctive features (through study of C-H vibration frequencies and proton coupling patterns), than with cyclopentadienyl complexes.

Although our preliminary NMR studies of the newly prepared Ind_2Hg derivative⁹ and of IndHgX^* ($X = \text{Cl}, \text{Br}$) were not conclusive, a comparison of their IR spectra, as well as those of Ind_4Sn and $\pi\text{-CpFe}(\text{CO})_2\text{Ind}$, with the spectra of π -indenyl complexes has allowed identification of the nature of the metal-carbon

* Ind stands for the indenyl radical C_9H_7 .

bond in these four complexes to be made, in agreement with the valence concepts for these molecules; identification by IR is less pronounced in the case of the corresponding cyclopentadienyl compounds.

RESULTS AND DISCUSSION

Preparation of indenylmercury compounds

(a). *IndHgX*

Though reported earlier¹⁰, these derivatives do not seem to have been well characterised. The chloride has been the subject of a more recent study¹¹; it was described as resulting from the action of IndLi on HgCl₂. Indenylsodium being, in our opinion, a more suitable intermediary than other metallated indenenes in the preparation of indenylmetal complexes, we tried its action mainly on HgCl₂ in THF and in other solvents. We found out that the preparation of IndHgCl can be successfully carried out with good yields only if THF is used as a solvent and if temperatures are around -80°.

IndHgCl when pure is a white crystalline solid (m.p. 150°); the bromide is rather yellowish (m.p. 130°). Both are stable to air and light, are soluble in THF, DMSO and DMF and are poorly soluble in benzene, chloroform and ether. They are completely insoluble in water, even at 100°, but are easily decomposed by HCl. In contrast, π -indenyl complexes are resistant both to water and to HCl. Solutions of IndHgX in THF resist hydrogenation in presence of Adam's catalyst even at high pressures; however, in ethanol they do absorb hydrogen without yielding any identifiable product. Under similar conditions, the phenyl ring in π -indenyl complexes is easily saturated, and tetrahydroindenyl derivatives are obtained.

(b). *Ind₂Hg*

This product seems to have eluded previous attempts for its isolation*. Action of excess IndLi or IndNa on HgCl₂ leads only to disproportionation with precipitation of metallic mercury.

It is well known, however, that organomercurials, RHgX, exist in equilibrium as follows¹²:



Consequently, addition to RHgX solutions of a compound capable of forming a stable anionic complex with HgX₂ (such as KI or KSCN) will favour the formation of R₂Hg. These reactions are usually conducted in alcohol.

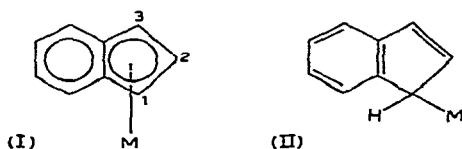
Repeated experiments to prepare Ind₂Hg from IndHgCl by this method led us to modify the procedure; satisfactory results were obtained only by the action of an aqueous solution of KI or of KSCN upon a suspension of IndHgCl in ether and then by evaporation of the ether layer. Ind₂Hg is an air- and light-sensitive crystalline powder (m.p. 130°); however it can be stored in dark under nitrogen. Its solubility and chemical behaviour are analogous to IndHgCl. It reacts with HgX₂ in organic solvents to give IndHgX.

* *Note added in proof.* Ind₂Hg has been recently reported also by F. A. Cotton and T. J. Marks (*J. Amer. Chem. Soc.*, 12 (1969) 3178). It was obtained by action of IndLi on HgCl₂ at -78°, and a study of its NMR spectrum showed it to be fluxional.

The compound obtained by our procedure (from highly purified IndHgCl) gave us an NMR spectrum at 30° identical to that reported by Cotton and Marks.

Infrared spectra

It is assumed that all the bands observed in the high and medium frequency region ($4000\text{--}500\text{ cm}^{-1}$) are exclusively due to internal vibrations (C-H and C-C stretching and bending modes) of the indenyl ligand. Because the vibrations of the phenyl ring are quite characteristic, only the C_5 ring will be considered. If structures



(I) and (II) are presumed to be most likely for π - and σ -indenyl complexes, their IR spectra should reflect the difference in ring symmetry for the following reasons:

(a). The vibrational representation of the π -bonded C_9H_7 group is:

$$\Gamma = 15A_1 + 6A_2 + 7B_1 + 14B_2$$

Out of the 42 possible vibrations, 6 are IR inactive, whereas all are active when the indenyl ligand is σ -bonded because of the total loss of symmetry.

(b). Due to the aromatic character of the C_5 ring in the π structure, all $\nu(C-H)$ stretching frequencies should lie above 3000 cm^{-1} . In the σ structure, the aliphatic carbon (in the 1-position) should show a $\nu(C-H)$ band lying between 2800 and 3000 cm^{-1} .

(c). By analogy with the π -cyclopentadienyl derivatives^{13,14}, one of the two $\gamma(C-H)$ (out of plane) vibrations in the π -structure is expected to lie at $700\text{--}850\text{ cm}^{-1}$.

In the σ -bonded indenyl ring, $\gamma(C_1-H)$ should occur around 700 cm^{-1} according to empirical observations such as in the spectra of 9-substituted fluorenyl derivatives¹⁵. As for $\gamma(C_2-H)$ and $\gamma(C_3-H)$, two bands should be observed around 700 cm^{-1} belonging to each of the two vibrations, C_2-H and C_3-H . In summation, the π -bonded indenyl ligand should show one $\gamma(C-H)$ band around $700\text{--}800\text{ cm}^{-1}$, while three bands would be expected in this region in the case of the σ -bonded ligand.

 π -Indenyl complexes

IR spectra of all the π -complexes which we examined, together with the data taken from the literature, lend further support to the above predictions regarding $\nu(C-H)$ and $\gamma(C-H)$ vibrations:

- (1). Bands of medium intensity assignable to aromatic C-H stretching vibrations of both C_5 and C_6 rings are observed in the $\nu(C-H)$ region only between 3000 and 3100 cm^{-1} .
- (2). $\gamma(C-H)$ vibrations of the C_6 and the C_5 rings are well separated; the former shows an intense band around 750 cm^{-1} (split sometimes) and the band due to the latter usually lies at higher frequencies (Table 1).

These are usually the most prominent sets of bands in the whole spectrum.

 σ -Indenyl complexes: IR spectra of $IndHgCl$ and Ind_2Hg

A tentative assignment of the most significant bands in the spectra of these compounds was made possible by comparison with the spectra of the π complexes on the one hand and by observation of band displacement in the spectra of the deuterated derivatives* on the other.

* Exchange of H_1 and H_3 only.

TABLE 1

INFRARED FREQUENCIES (IN cm^{-1}) OF C-H OUT-OF-PLANE VIBRATIONS IN THE 850 TO 700 cm^{-1} REGION IN SOME INDENYL AND CYCLOPENTADIENYL COMPLEXES

Compound	C-H phenyl ring	C-H C_5 -ring
Ind_2Fe	726, 740	804
$\text{Ind}_2\text{TiCl}_2$	738, 750	852, 860
$\text{Ind}_2\text{ZrCl}_2$	745	830
Cp_2Fe		815
Cp_2TiCl_2		830

(a). The 3000 cm^{-1} region. The $\nu(\text{C-H})$ region of IndHgCl contains, besides the medium bands at 3050–3060 cm^{-1} due to aromatic C-H, two well-separated bands also of medium intensity at 2920 and 2850 cm^{-1} (Fig. 1) which we attribute to

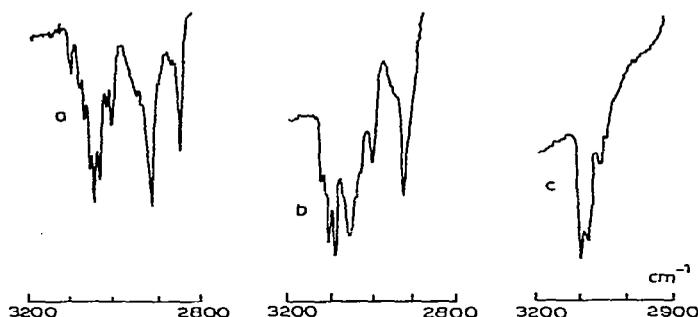


Fig. 1. Infrared spectra in the C-H stretching region of IndHgCl (a), $\pi\text{-CpFe}(\text{CO})_2\text{-}\sigma\text{-Ind}$ (b) and $(\pi\text{-Ind})_2\text{-TiCl}_2$ (c) taken as mulls in hexachlorobutadiene.

$\text{C}_1\text{-H}$ stretching vibrations (of the carbon bonded to mercury). Partial exchange of H with D ($\approx 75\%$) caused a corresponding decrease in their intensity. Normally, one would expect only one band; however, in the present case, we suggest that the second band is due to different environments of the C-H bonds in the crystal unit cell. Out of the two corresponding bands (2870 and 2830 cm^{-1}), in the case of IndHgBr , the one at lower frequency is relatively less intense.

A σ structure in these compounds seems, therefore, to be most likely on the basis of the above observations.

(b). The 800 to 500 cm^{-1} region. The spectrum between 800 and 700 cm^{-1} exhibits bands of high intensity; their shape and number allow a clear-cut distinction between π - and σ -bonded indenyl complexes. Thus, the phenyl band at 750 cm^{-1} is flanked by two equally intense bands at 788 and 718 cm^{-1} ; a third one of lower intensity lies at 655 cm^{-1} (Fig. 2).

It is possible to assign each band to the corresponding C-H vibrator on the basis of the following arguments:

- (1). The band at 788 cm^{-1} is due to $\gamma(\text{C}_3\text{-H})$ (deformation). It completely disappears in the deuterated derivative, and the corresponding C-D band is shifted to 600 cm^{-1} (in the ratio of 1.31).
- (2). The band at 718 cm^{-1} is due to $\gamma(\text{C}_2\text{-H})$. Since this hydrogen does not exchange

with deuterium, the band retains its intensity in the deuterated derivative; only its frequency gets slightly shifted (to 724 cm^{-1}).

- (3). The 655 cm^{-1} band is probably due to $\gamma(\text{C}_1\text{-H})$. Methylene rocking vibrations may occur at 690 cm^{-1} ; thus a band at 692 cm^{-1} due to CH_2 occurs in indene itself. In 9-monodeuterated fluorene, Scherf and Brown¹⁵ observed a shifting of this band to 677 cm^{-1} , and they attributed it to the remaining $\text{D}-\overset{\text{I}}{\underset{\text{I}}{\text{C}}}-\text{H}$.

By analogy, it can be assumed that the substitution of one of the methylene hydrogens by a heavy metal (Hg) shifts the $\text{C}_1\text{-H}$ band to lower frequencies as observed (655 cm^{-1}). This band also disappears in the deuterated derivative.

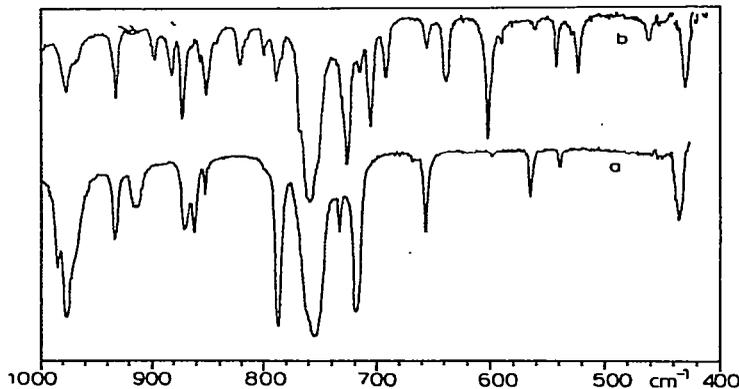


Fig. 2. Infrared spectra in nujol of IndHgCl (a) and of the partially deuterated derivative (b) (on positions C_1 and C_3) in the 1000 to 400 cm^{-1} region.

The spectra of IndHgCl and of the partially deuterated derivative are shown in Fig. 2. In addition two bands at 970 and 860 cm^{-1} can be attributed to $\delta(\text{C-H})$; both are shifted to 702 and 636 cm^{-1} , respectively, in the deuterated compound.

Other bands. In conclusion we have been able to characterise an intense band at 315 cm^{-1} assignable to Hg-Cl; with the bromide it appears at 244 cm^{-1} , and its intensity is considerably reduced. These Hg-X attributions are in agreement with the band assignments in benzyl mercuric halides¹⁶.

The IR spectrum of Ind_2Hg is very similar to that of IndHgCl and does not require any special comment.

The agreement between the measured spectra of IndHgCl and of Ind_2Hg and the predictions put forth for a σ -bonded indenyl radical afford a reliable proof for the existence of a $\sigma(\text{Hg-C})$ bond in these compounds as distinct from the delocalised π -bonding between the indenyl radical and a transition element.

A further confirmation is provided by the analogy of the IR spectra of Ind_4Sn and of $\pi\text{-CpFe}(\text{CO})_2\text{-}\sigma\text{-Ind}$ with those of indenylmercuric compounds.

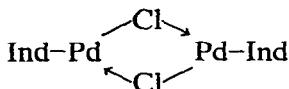
¹H NMR spectra

Poor solubility of IndHgCl in chloroform prevented us from obtaining well-resolved spectra. However, in spite of high solubility in DMSO, the spectrum at 60 MHz was not reproducible; the relative intensities of the C_5 -ring and C_6 -ring proton signals varied in different measurements. Nevertheless, a broad signal was observed in most cases at 4.4 ppm (in DMSO), attributable to H_1 and lying at higher field than

the singlet at 6.82 ppm (probably due to H₂ and H₃) and the phenyl multiplet (7 to 7.9 ppm). These spectra are being further investigated; preliminary results have been published recently¹¹ by other workers.

Indenylpalladium derivative

Our investigation of further indenyl derivatives led us to prepare a new palladium compound which may be formulated on the basis of measurements of molecular weight as:



The ¹H NMR spectrum of the product in DMSO-*d*₆ (the compound is poorly soluble in chloroform) shows a doublet at 6.3 ppm and a multiplet at 6.9 to 7.3 ppm, of an intensity ratio 2 to 5. It can be considered as an AB₂ spectrum of a π-bonded indenyl compound, the triplet due to H₂ being shifted to low fields and confounded with the phenyl protons multiplet.

However, the IR spectrum in the ν(C-H) region shows bands at 2960, 2930 and 2870 cm⁻¹, indicating a σ-type structure.

In view of the unusual behaviour of the palladium aromatic compounds, the nature of the palladium-indenyl bond in this compound cannot be established with certainty from the present available data.

Conclusion

IR measurements provide a useful means for distinguishing between π- and σ-indenylmetal compounds, whereas vibrational studies made on cyclopentadienyl derivatives do not seem to be as informative about the type of metal-to-ring bonding in view of the greater number of C-H vibrators. Nevertheless, it is safe to argue that for the same metal, the bonding is of the same nature in both types of compounds. In other words, if indenylmercury or indenyltin compounds are σ-complexes, as we tried to prove by the present study, then the same can be said about their cyclopentadienyl homologues.

EXPERIMENTAL

Preparation of IndHgX

20 g (0.74 mmole) of HgCl₂ were dissolved in 30 ml of THF (distilled on LiAlH₄) and were cooled to -80° in a dry-ice bath. A solution of IndNa in 30 ml of THF (1 mole of IndNa per mole of HgCl₂) was progressively added with vigorous stirring during a period of 1 h. A voluminous precipitate was formed at the end of the reaction. The mixture was brought to room temperature, and most of the THF was evaporated under vacuum. Ethyl ether was then introduced, and the resulting suspension was filtered. Soxhlet extraction of the solid with benzene or chloroform yielded 23 g (90% of theory) of a light cream-coloured crystalline compound. Further recrystallisation gave a pure white product (m.p. 150°). (Found: C, 28.96; H, 2.2. C₉H₇ClHg calcd.: C, 30.8; H, 1.99%.)

IndHgBr was similarly prepared from HgBr₂, though with lower yields. It is yellowish in colour (m.p. 130°) (Found: C, 27.10; H, 1.85; Br, 20.06. C₉H₇BrHg calcd.: C, 27.40; H, 1.77; Br, 20.02%.)

Preparation of Ind₂Hg

This was easily obtained by shaking an ethereal suspension of IndHgCl (or the bromide) with a saturated aqueous solution of KI or KSCN in a separatory funnel. The ether solution was decanted, dried and then concentrated. The resulting yellow powder (m.p. 130°) was recrystallised in chloroform under nitrogen. It blackens upon prolonged exposure to air and light. (Found: C, 48.25; H, 3.53; Cl, 0.0. C₁₈H₁₄Hg calcd.: C, 49.25; H, 3.23%.)

Preparation of deuterated IndHgCl

Deuterated indene, required for the preparation, was obtained from ordinary indene by three successive metallations with Na, followed by hydrolysis of the resulting IndNa in D₂O. NMR spectrum of the final product showed a residue of unexchanged protons in the following proportions: H₁ 15%, H₂ 100% (no exchange with D), H₃ 25%.

Preparation of IndPdCl

IndNa in THF was added to a solution of 5 g of anhydrous PdCl₂ in 50 ml of THF (1 mole of IndNa per mole of PdCl₂) at 0° with continued stirring. After 1 h, THF was removed under vacuum (not to complete dryness), and the residue was treated with ether and was filtered. Concentration of the filtrate gave a dark brown crystalline compound which was identified as (IndPdCl)₂. (Found: C, 43.91; H, 3.05; Cl, 13.19; mol. wt. ebulliometric in benzene, 535. C₁₈H₁₄Cl₂Pd₂ calcd.: C, 42.06; H, 2.75; Cl, 13.80%; mol. wt. 514.) The product was recrystallised with difficulty. It is poorly soluble in chloroform or benzene, is quite soluble in DMSO, pyridine.

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