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Interaction between $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{OsH}]^+\text{PF}_6^-$ and nitrogen or oxygen bases. Hydrogen bonds of the type $[\text{OsH}]^+ \cdots \text{B}$

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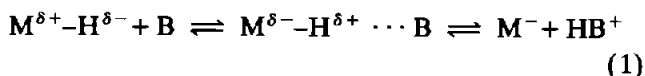
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Abstract

The interactions between the synthesized salt $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{OsH}]^+\text{PF}_6^-$ (**1**) and N or O bases were studied by IR spectroscopy. Hydrogen-bond formation of the type $[\text{OsH}]^+ \cdots \text{B}$ occurs prior to proton transfer if phosphoryl compounds (Ph_3PO , Fc_3PO , $(\text{Me}_2\text{N})_3\text{PO}$) are used as bases. In the last case is revealed the equilibrium between such a complex and the product of deprotonation of **1** in solution. There is no evidence for hydrogen-bond formation if **1** is deprotonated by the N bases (Et_3N , Py).

1. Introduction

Considerable attention has been focussed recently on the deprotonation of transition-metal hydrides [1–4]. It has been suggested that the proton transfer proceeds through hydrogen-bonded intermediates [2,4]. At this stage the polarization $\text{H}^{\delta-}\text{-M}^{\delta+}$ changes before proton transfer:



The interaction between $\text{HCo}(\text{CO})_4$ and O and N bases in acetonitrile solution and in matrices, in a search for hydrogen bonding, was examined by IR and Raman spectroscopy [4], but these attempts were unsuccessful.

The object of the present work was to examine the interaction between hydrodobis(pentamethylcyclopentadienyl)osmium hexafluorophosphate $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{OsH}]^+\text{PF}_6^-$ (**1**) and different nitrogen and oxygen bases, using IR spectroscopy. Compound **1** is convenient for such a study. The permethylated cyclopentadienyl ligands, in contrast to the carbonyl ones, have no bands in the region of the metal–hydrogen stretching vibrations (M–H). Furthermore, the positive charge should (by analogy with organic compounds) favour

hydrogen-bond formation. It is also hardly probable that the total positive charge on the cation would change the direction of the M–H bond polarization. This suggestion is consistent with the high-field ^1H NMR spectrum of **1** which shows a hydride resonance at $\delta = -15.6$, *i.e.* in the region shared with neutral hydrides [5–6].

Compounds differing in basicity and in ability to form hydrogen bonds were chosen as proton acceptors, namely Et_3N , Py, Ph_2NH (N bases) and Ph_3PO , Fc_3PO , $(\text{Me}_2\text{N})_3\text{PO}$ (O bases). Phosphine oxides were used because they have rather low basicity and a great capacity for formation of hydrogen bonds.

2. Results and discussion

IR spectra of **1** were studied in the solid state and in different solvents. The position of the $\nu(\text{Os-H})$ band in the solid state is 2164 cm^{-1} with a weak high-frequency shoulder (2194 cm^{-1}) (Fig. 1) The maximum of this stretching vibration in the diluted CH_2Cl_2 solution occurs at $2195\text{--}2200\text{ cm}^{-1}$ with a low-frequency shoulder of 2164 cm^{-1} . The difference may be safely explained by contact-ion-pair formation in the solid state. The band $\nu(\text{Os-H})$ is weak and broad. The value of the integral intensity is $0.36 \times 10^4\text{ l mol}^{-1}\text{ cm}^{-2}$ in CH_2Cl_2 ; $\Delta\nu(1/2)$ is $60\text{--}65\text{ cm}^{-1}$.

The interaction of the compound studied with a strong base such as Et_3N causes the proton transfer. If

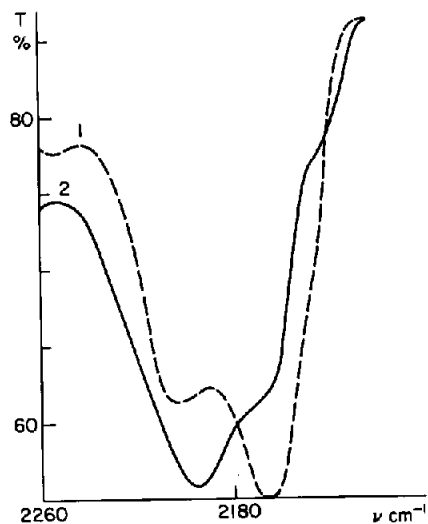


Fig. 1. IR spectra in the $\nu(\text{M-H})$ range of the $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{OsH}]^+\text{PF}_6^-$ in the solid state (curve 1) and in CH_2Cl_2 solution (curve 2) ($8.0 \times 10^{-2} \text{ mol l}^{-1}$, $d = 4 \text{ mm}$).

the spectra of 1 are measured in an excess of Et_3N in solution, the band of $\nu(\text{Os-H})$ is not observed, but bands characteristic of the protonated base are manifest. The IR spectrum of the second product of deprotonation is identical to that of decamethylsmocene (Fig. 2).

In a similar manner, the interaction between 1 and Py brings about deprotonation. The observed H-Os stretches offer no evidence for hydrogen-bond forma-

tion. As the concentration of Py in the solution of 1 increases, the intensity of the $\nu(\text{Os-H})$ band decreases and bands attributed to the pyridinium salt vibrations appear. This assignment was supported by comparison with the spectrum of the specially synthesized salt $\text{PyH}^+\text{PF}_6^-$. Thus, transfer of protons from 1 to the strong N bases (Py, Et_3N) takes place. The intermediate hydrogen-bonded complexes are not revealed, as in the cases of $\text{HCo}(\text{CO})_4$, $\text{HRe}(\text{CO})_5$ and $\text{HMn}(\text{CO})_5$ [4].

A decrease in the basicity of nitrogen bases, *i.e.* the use of diphenylamine as a proton-acceptor, does not lead to observed perturbation of hydrogen bonding. The position and intensity of the $\nu(\text{OsH})$ band remain unchanged, when compound 1 is treated with an excess of Ph_2NH . This indicates the absence of appreciable interaction between the salt 1 and this base.

It was advantageous to use such proton acceptors as Ph_3PO , Fc_3PO and $(\text{Me}_2\text{N})_3\text{PO}$ (HMP) because the basicities of these phosphorus compounds are less than those of Et_3N and Py, but the formation constants (K_f) of hydrogen bonds are greater by a factor of 10 or 15 ($\log K_f$ with phenol > 3) (Table 1) [7,8]. It has also long been known that the $\nu(\text{P=O})$ bands are sensitive to hydrogen-bond formation [9,10].

IR spectral investigation of the interaction between the compound 1 and these bases in the two regions, *i.e.* $\nu(\text{P=O})$ and $\nu(\text{OsH})$ were what enabled us to find the hydrogen bond of type $\text{OsH} \cdots \text{O=P}$. We observed the decreasing intensity of the $\nu(\text{P=O})$ bands and the appearance of new low-frequency ones if the phosphoryl

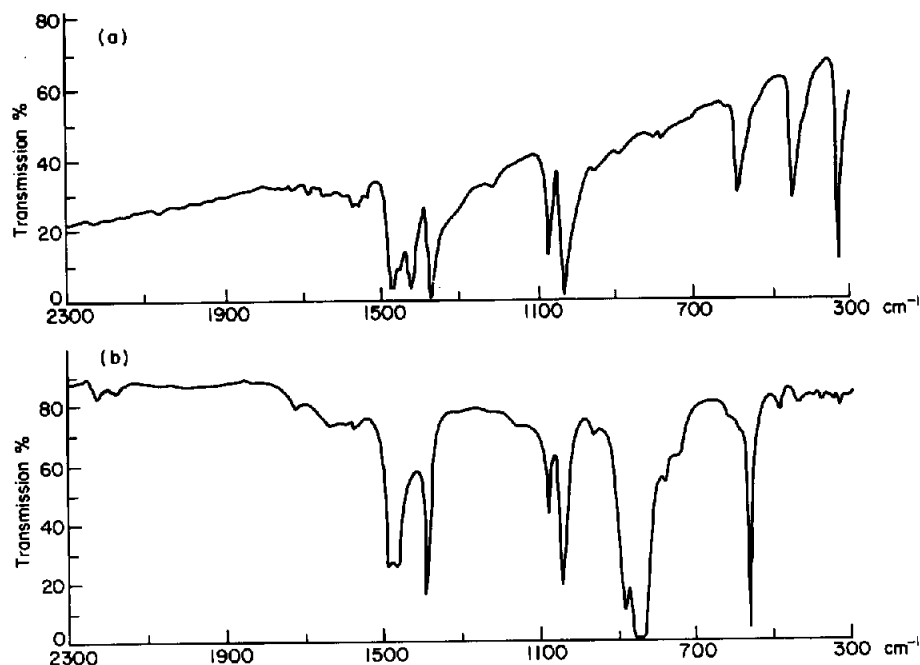


Fig. 2. IR spectra of (a) $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Os}$; (b) $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{OsH}]^+\text{PF}_6^-$ (KBr pellets).

TABLE 1. Formation constants of the hydrogen bonds (K_f) and $\text{p}K_a$ of N and O bases chosen. Literature reference numbers are in square brackets

Bases	$\log K_f$	$\text{p}K_a$
Et_3N	2.0 [7]	18.5 [9] in CH_3CN
Py	1.6 [7]	12.3 [9] in CH_3CN
Ph_3PO	3.0 [8]	2.8 [10] in CH_3NO_2
Fc_3PO	3.6 [8]	—
$(\text{Me}_2\text{N})_3\text{PO}$	3.5 [7]	6.1 [10] in CH_3NO_2

compound solutions in CH_2Cl_2 contained an excess of salt 1. In the spectra of Ph_3PO (Table 2), the new weak $\nu(\text{P}=\text{O})$ band at 1167 cm^{-1} is exhibited in addition to the fundamental one (at 1193 cm^{-1}). The changes in the spectra of Fc_3PO and HMP appeared to be more pronounced, and this agrees with the enhancement of their H-bond stability and of the values of K_f with phenol (Table 1). In the last case, the interaction with 1 causes the disappearance of the $\nu(\text{free PO})$ band (Table 2).

In the $\nu(\text{OsH})$ region the interaction resulted in the increase of the intensity and half-width of the band (Fig. 3). Thus, its integral intensity is doubled if the hydrogen bond with Ph_3PO is formed ($A(\text{OsH}) = 0.6 \times 10^4\text{ l mol}^{-1}\text{ cm}^{-2}$). In the case of HMP the low-frequency shift of the $\nu(\text{OsH})$ band is revealed ($\Delta\nu = 20\text{ cm}^{-1}$). However, growth of the HMP concentration is accompanied by a decrease in the integral intensity of the band. The most likely explanation is that the process does not stop at hydrogen-bond formation, but is followed by proton transfer. To shift the equilibrium (1) to the left we measured the spectra at lower temperatures (Fig. 4). It turned out that the intensity of the $\nu(\text{OsH})$ band in this case increases several times. The value of $A(\text{OsH})$ at -60°C is $1.8 \times 10^4\text{ l mol}^{-1}\text{ cm}^{-2}$, *i.e.* five times as great as that without HMP. Thus, the observed decrease of the intensity was in fact caused by proton transfer to this phosphoryl compound (which is more basic than the others). Consequently, the interaction of compound 1 with HMP leads not only to a low-frequency shift, but also to enhancement of intensity characterizing the hydrogen-bonded complexes.

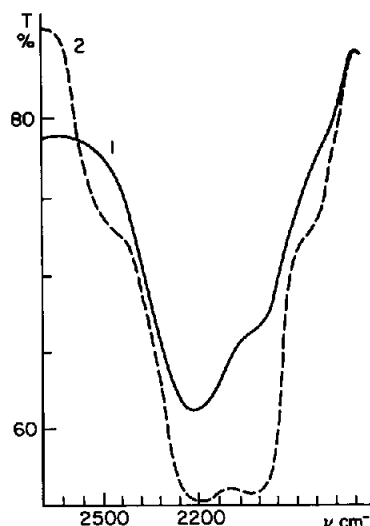


Fig. 3. IR spectra of $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{OsH}]^+ \text{PF}_6^-$ (curve 1) ($8.0 \times 10^{-2}\text{ mol l}^{-1}$) and $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{OsH}]^+ \text{PF}_6^- + \text{Ph}_3\text{PO}$ (curve 2) ($2.0 \times 10^{-1}\text{ mol l}^{-1}$) in CH_2Cl_2 solution.

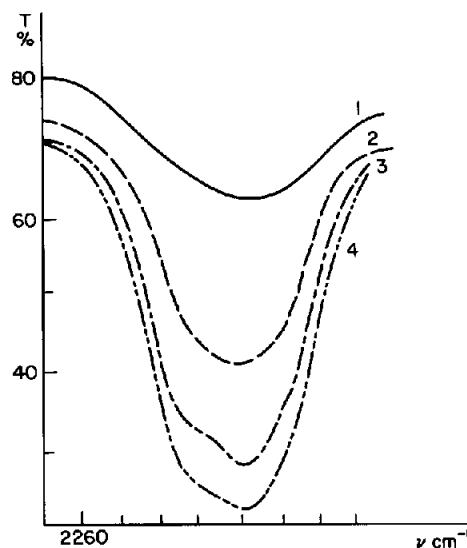


Fig. 4. IR spectra of $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{OsH}]^+ \text{PF}_6^- + \text{HMP}$ in CH_2Cl_2 solution at different temperatures: curve 1, 20°C ; curve 2, 0°C ; curve 3, -20°C ; curve 4, -60°C .

TABLE 2. IR spectra of phosphoryl compounds in $\text{CCl}_4:\text{CH}_2\text{Cl}_2$ (1:1) and in this solvent with excess of the salt 1

Ph_3PO	$\text{Ph}_3\text{PO} + 1$	Fc_3PO	$\text{Fc}_3\text{PO} + 1$	HMP	HMP + 1	Assignment
1193vs	1193s	1211s	—	1204vs	—	$\nu(\text{free PO})$
—	1177s	1177s	1188s	—	—	—
—	1167w	—	1121s	—	1187vs	$\nu(\text{bonded PO})$

The following conclusion can be reached. We succeeded at first in identifying the hydrogen bond between the cationic transition metal hydride and bases $[(\text{Cp}^{10}\text{OsH})^+ \cdots \text{B}]$ as the stage prior to proton transfer. The formation of such a (probably weak) hydrogen bond is indicated if the bases chosen possess a great ability to form hydrogen-bonded complexes. The results obtained call for new research. Thus, it is of importance to investigate the interaction of neutral hydrides with such bases. Our experimental results provide a stimulus to theoretical studies. It would be very interesting to elucidate the potential surface of proton transfer and the sign of the charge on the hydrogen atom of the M–H bond in cationic complexes. These problems are under active investigation.

3. Experimental details

Compound 1 was obtained by mixing 70% $\text{HPF}_6(\text{aq})$ and osmocene solution in absolute ether. The precipitate formed was filtered. Further purification was by precipitation with ether from methylene chloride solution.

Anal. Found: C, 38.42; H, 5.70; Os, 31.62; P, 5.70; F, 18.29. $\text{C}_{20}\text{H}_{31}\text{FOsP}$ calc.: C, 39.60; H, 5.11; Os, 31.62; P, 5.11; F, 18.79%. ^1H NMR (CD_2Cl_2): δ 2.00 (30H, C_5Me_5), -15.59 (1H, HOs). ^{13}C NMR (CH_2Cl_2): δ 90.91 (C_5Me_5), 9.35 (C_5Me_5).

The spectra were recorded with Specord M-80 and M-82 IR spectrophotometers. Measurements were made in the solid state (KBr) and in CH_2Cl_2 and

$\text{CH}_2\text{Cl}_2:\text{CCl}_4$ (1:1) solutions. Concentrations were varied in the range 5×10^{-2} – 5×10^{-3} mol l^{-1} .

The frequency $\nu(\text{Os-H})$ 2165 cm^{-1} calculated from the equation given in ref. 13 agreed with the experimental frequency.

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