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# The role of hydrogen bonds involving the metal atom in protonation of polyhydrides of molybdenum and tungsten of $MH_4(dppe)_2$

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## Abstract

The interactions of polyhydrides of molybdenum and tungsten of the type  $MH_4(dppe)_2$  with proton donors of different protonation ability were studied with IR and UV spectroscopy in  $CH_2Cl_2$ . It was found that the formation of a molecular hydrogen-bonded complex ( $OH \cdots M$ ) (1) is the first stage of protonation. An ionic H-complex of the type  $M^+H \cdots O^-$  (2) was formed as a result of proton transfer. Deprotonation of  $[WH_5(dppe)_2]^+X^-$  salt was found to proceed through the intermediate formation of complexes 2 and 1.

**Keywords:** Molybdenum; Tungsten; Hydrogen bonding; Protonation; Infrared spectroscopy

## 1. Introduction

Protonation reactions of molybdenum and tungsten compounds have attracted considerable attention in recent years because of their importance as the first stage of many catalytic processes [1,2].

Attachment of protons and the formation of relatively stable cationic hydrides is a rather common reaction of coordinatively unsaturated phosphinehydride complexes of transition metals [3]. For polyhydrides of tungsten, stable  $[WH_5(dppe)_2]^+X^-$  type salts have been isolated [3]. Analogous salts of molybdenum have not been isolated. However, their formation has been proposed in articles concerned with protonation kinetics [4].

We have recently shown that for a number of  $\pi$ -complexes of Group VIII transition metals ( $Cp_2M$ ,  $Cp_2^*M$ ,  $M = Ru, Os$  and  $Cp^*M(CO)_2$ ,  $M = Ir, Rh$ ) protonation in low-polar media proceeds through the consecutive formation of molecular  $M \cdots OH$  (1) and ionic  $MH^+ \cdots O^-$  (2) complexes involving the metal atom [5–8].

To establish the possibility of hydrogen bond formation involving Mo and W atoms the interaction of polyhydride complexes of molybdenum and tungsten

$MH_4(dppe)_2$  with proton donors of different protonation ability was studied by IR and UV spectroscopy. As proton donors,  $C_6H_5OH$ ,  $(CF_3)_2CHOH$ ,  $CF_3COOH$  (TFA) were used.

## 2. Results and discussion

The interaction of polyhydrides with weak proton donors ( $C_6H_5OH$ ,  $(CF_3)_2CHOH$ ) in  $CH_2Cl_2$  led to

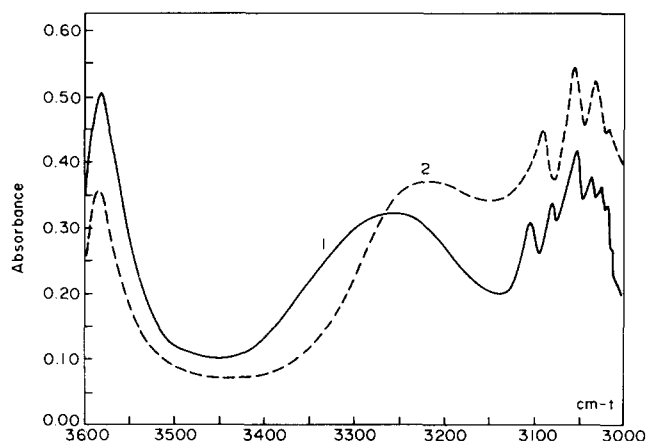
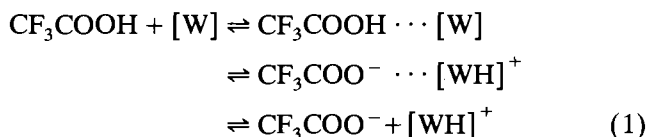


Fig. 1. IR spectra in range  $\nu_{OH}$  for  $C_6H_5OH$  ( $C = 10^{-3} \text{ mol l}^{-1}$ ) plus  $MH_4(dppe)_2$  ( $C = 3 \times 10^{-2} \text{ mol l}^{-1}$ ) ( $M = Mo$  (curve 1),  $W$  (curve 2)) in  $CH_2Cl_2$   $d = 0.1 \text{ cm}$ .

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molecular hydrogen-bonded complexes. The bands of stretching vibrations of bonded hydroxy groups appeared in the range 3180–3300  $\text{cm}^{-1}$  (Fig. 1). The intensity of these bands increased on cooling. The position of these bands, dependent on the metal atom, provided the identity of ligands. The value of frequency shifts  $\Delta\nu(\text{OH}) = [\nu(\text{free OH}) - \nu(\text{bonded OH})]$  of  $\Delta\nu(\text{OH} \cdots \text{W})$  is greater than  $\Delta\nu(\text{OH} \cdots \text{Mo})$  for all proton donors. Such sensitivity of stretching vibration of bonded OH groups to the nature of the metal was attributed to the formation of intermolecular hydrogen bonds with the metal atoms. These hydrogen bonds are rather strong; the values of  $\Delta H$  were 5–7  $\text{kcal mol}^{-1}$  respectively. The ‘factors of basicity’ ( $E_j$ ) of the metal atom in the hydrogen bond remain constant on changing the proton donors. The values of  $E_j$  increase down the group ( $E_j = 1.10$  for  $M = \text{Mo}$ ,  $E_j = 1.19$  for  $M = \text{W}$ ) as in  $\pi$ -complexes of transition metals of Group VIII [7].

The interaction of  $\text{WH}_4(\text{dppe})_2$  with the strong proton donor TFA results in partial proton transfer. In the case of  $\text{CF}_3\text{COOH}$  it is possible to observe bands of molecular  $\text{CF}_3\text{COOH} \cdots [\text{W}]$  (1) ( $1730 \text{ cm}^{-1}$ ) and ionic  $\text{CF}_3\text{COO}^- \cdots [\text{HW}]^+$  complexes (2) ( $1705 \text{ cm}^{-1}$ ), and of  $\text{CF}_3\text{COO}^-$  anion ( $1685 \text{ cm}^{-1}$ ) in the range of  $\nu\text{OCO}$  vibrations of TFA [7] (Fig. 2). This allowed study of the following equilibrium



The equilibrium shifted to the ionic complex 2 with decreasing temperature (295–220 K). A protonated species was also detected in the IR spectra  $\nu\text{WH}$  and in the UV spectra. The characteristic bands of the nonprotonated complex in the UV spectrum at 390 nm

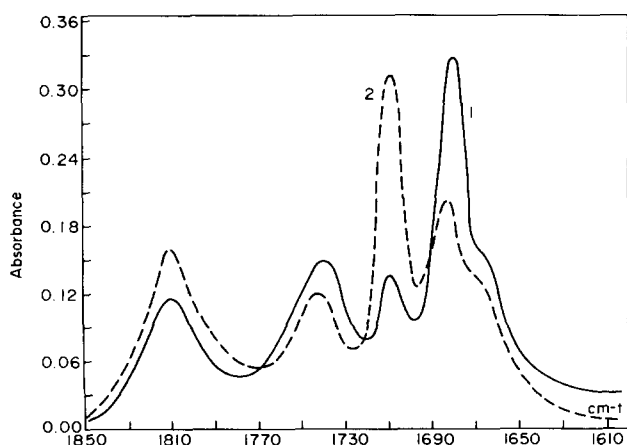


Fig. 2. IR spectra of  $\text{CF}_3\text{COOH}$  ( $10^{-3} \text{ mol l}^{-1}$ ) plus  $\text{WH}_4(\text{dppe})_2$  ( $C = 10^{-2} \text{ mol l}^{-1}$ ) in  $\text{CH}_2\text{Cl}_2$   $d = 0.1 \text{ cm}$  at 293 K (curve 1) and 213 K (curve 2).

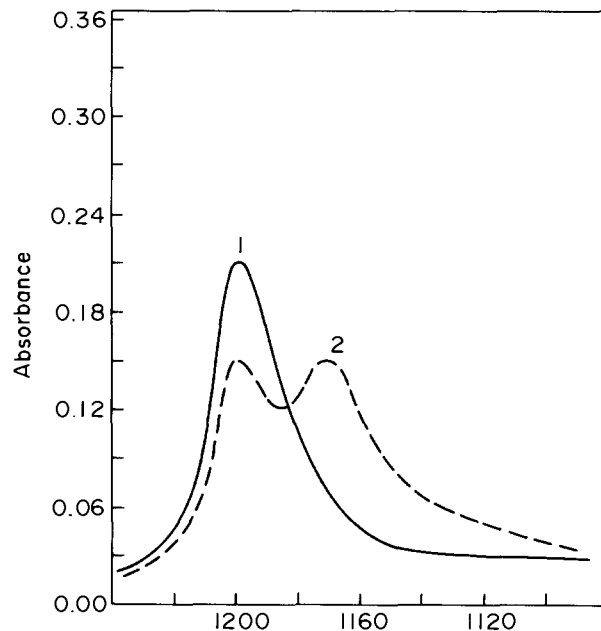


Fig. 3. IR spectra of HMPA in range  $\nu\text{PO}$  in  $\text{CH}_2\text{Cl}_2$   $\nu\text{PO}(\text{free})$  (curve 1), plus  $\text{WH}_4(\text{dppe})_2$  ( $C = 10^{-2} \text{ mol l}^{-1}$ )  $d = 0.1 \text{ cm}$  (curve 2).

and in the IR spectrum at  $1770 \text{ cm}^{-1}$  disappeared while a band appeared at  $1880 \text{ cm}^{-1}$ . This new band coincides with  $\nu(\text{WH}^+)$  of  $[\text{WH}_5(\text{dppe})_2]^+ \text{X}^-$  ( $\text{X} = \text{BPh}_4, \text{HCl}_2$ ) salt solutions.

The same complexes 1 and 2 were detected in the reverse process of deprotonation. The spectra of the protonated salts mixed with  $\text{K}^+ \text{CF}_3\text{COO}^-$  (TFAK) in the presence of 18-crown-6 in  $\text{CH}_2\text{Cl}_2$  were measured in the range 2000–1600  $\text{cm}^{-1}$ . The bands of molecular (1) and ionic (2) complexes were observed as well as the weak band of TFA (free) vibration. So treatment of salt with TFAK results in a decreasing of the  $\nu(\text{WH})$  cation band ( $1820, 1880 \text{ cm}^{-1}$ ) intensity and the appearance of a new band of  $\nu(\text{WH})$  in tungsten polyhydride ( $1785 \text{ cm}^{-1}$ ). Similarly, in the UV spectrum a band attributed to the  $d-d$  transition of tungsten electrons in the nonprotonated polyhydride appeared. On decreasing the temperature to 240 K the band intensity of the ionic complex 2 increased.

Thus, the proton transfer in protonation or deprotonation of the tungsten polyhydride proceeds through the system of hydrogen-bonded complexes 1 and 2 similarly to that found for metallocenes of the Fe subgroup [6–8].

Unfortunately, unlike  $\nu(\text{OsH})$  [8], the range of  $\nu(\text{WH})$  stretching vibration ( $1900\text{--}1800 \text{ cm}^{-1}$ ) appeared to be uninformative because of the presence of overtones of phenyl ring vibrations in this range.

Interaction of  $[\text{WH}_5(\text{dppe})_2]^+ \text{X}^-$  salt with a neutral base  $((\text{CH}_3)_2\text{N})_3\text{PO}$  (HMPA) results in the formation of the ion-molecular hydrogen-bonded complex  $[\text{WH}_5]^+ \cdots \text{O}=\text{P}$ . The presence of such a complex was

established by the IR spectrum in the range of the stretching vibration of P=O groups – a decrease of  $\nu(\text{PO free})$  1200  $\text{cm}^{-1}$  band intensity and the appearance of a low-frequency band of a hydrogen bond with a P=O group (1175  $\text{cm}^{-1}$ ) was observed (Fig. 3).

The case of  $\text{MoH}_4(\text{dppe})_2$  and its deuterio analogue  $\text{MoD}_4(\text{dppe})_2$  appeared to be rather different. It was necessary to use the last one for the study of  $\nu\text{OCO}$  vibrations of TFA because the  $\nu\text{MH}$  bands of  $\text{MoH}_4(\text{dppe})_2$  occur in the same range (1727, 1773, 1810  $\text{cm}^{-1}$ ). Protonation of these compounds with TFA proceeded at room temperature with the evolution of hydrogen. Low temperature prevented the hydrogen evolution and it became possible to observe the formation of molecular (1) and ionic (2) complexes and the anion as well as the tungsten analogue. At 240 K the spectrum of TFA in presence of  $\text{MoD}_4(\text{dppe})_2$  in  $\text{CH}_2\text{Cl}_2$  revealed bands of molecular (1730  $\text{cm}^{-1}$ ) and ionic (1708  $\text{cm}^{-1}$ ) complexes and of the anion (1686  $\text{cm}^{-1}$ ).

Thus, we have found for the first time the formation of a hydrogen bond of the type  $\text{OH} \cdots \text{M}$  with metals of Group VI. It has been shown that protonation of polyhydrides  $\text{MH}_4(\text{dppe})_2$  occurs in the system of hydrogen-bonded complexes of molecular and ionic types and deprotonation of respective salts involves the same H-complexes 1 and 2.

### 3. Experimental details

The compounds studied were prepared by published procedures [3,9,10].

Spectra were measured with Specord M-40 (UV, visible), M-80 and M-82 (IR) instruments. The concentrations of the molybdenum and tungsten complexes in  $\text{CH}_2\text{Cl}_2$  were varied in the range  $5 \times 10^{-2}$ – $5$

$\times 10^{-3}$  mol  $\text{l}^{-1}$ ; concentrations of proton donors were  $1 \times 10^{-3}$ – $1 \times 10^{-1}$  mol  $\text{l}^{-1}$ . Enthalpies of hydrogen bond formation  $\Delta H$  were calculated following the equation

$$\Delta H = 18\Delta\nu / (\Delta\nu + 720) \quad (2)$$

The factors of basicity  $E_j$  were estimated as described earlier [7].

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