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How can the metal affect the proton transfer to the dihydrides $[\{P(CH_2CH_2PPh_2)_3\}MH_2]$ (M = Fe, Ru, Os)? A low-temperature electronic spectroscopy study

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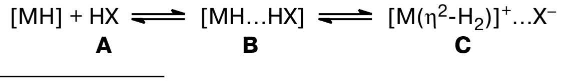
According to low-temperature UV-Vis spectroscopy data, the two-step protonation of iron subgroup metal hydrides $[\{P(CH_2CH_2PPh_2)_3\}MH_2]$ (M = Fe, Ru, Os) with *p*-nitrophenol includes the formation of ion pairs stabilized by a hydrogen bond between the cationic dihydrogen complex and the phenolate anion. The trend of the extent of proton transfer appeared to be aperiodic, FeH $\ll$ OsH $<$ RuH, in contrast to the previously obtained sequence of the proton-acceptor capacity of the hydride ligand, which increases down the group.

Key words: iron subgroup hydrides, electronic spectroscopy, dihydrogen bonding, proton transfer, ion pairs.

Recently, it was shown[1—3] that low-temperature protonation of transition metal hydrides with weak acids includes the intermediate formation of a new type of hydrogen bond, MH...HX, called dihydrogen bond[2,3] (DHB), preceding proton transfer to the hydride ligand and generation of the cationic dihydrogen complex.[4—6] The thermodynamic characteristics and the complete energy profile of the protonation reaction for some hydride(carbonyl) ruthenium(II) and rhenium(I) complexes with the tripodal $[MeC(CH_2PPh_2)_3]$ ligand have been reported.[5,6] In a recent study,[7] we showed that low-temperature protonation of the octahedral dihydrides $[\{P(CH_2CH_2PPh_2)_3\}MH_2]$ (M = Fe (**1**), Ru (**2**), Os (**3**)) using fluorinated alcohols as hydrogen donors results in dihydrogen complexes. The first step of the reaction affords DHB **B** (Scheme 1), whose strength steadily increases depending on the nature of the metal atom down the group.

Scheme 1



$$\underset{\textbf{A}}{[MH] + HX} \rightleftharpoons \underset{\textbf{B}}{[MH...HX]} \rightleftharpoons \underset{\textbf{C}}{[M(\eta^2\text{-}H_2)]^+...X^-}$$

It was of interest to find out whether this reaction involves the formation of ion pairs **C** stabilized by the hydrogen bond between the $(\eta^2\text{-}H_2)$-complex and the anion of the XH acid and how the nature of the metal atom influences the second step of the process. This was done using UV-Vis spectroscopy, which has been successfully used to study proton transfer to organic bases. Due to the remarkably different long-wave UV-Vis bands of the neutral and ionic forms,[8—10] nitrophenols are convenient indicators for protonation.

In this work, we studied the protonation of dihydrides **1**—**3** by low-temperature electronic spectroscopy. As the XH acid, we chose *p*-nitrophenol as it exhibits proton-donor ability and acidity comparable to those of the alcohol $(CF_3)_3COH$ ($P_i = 1.27$ and 1.33,[2] pK_a = 10.8 and 10.7 in DMSO,[11] respectively). Therefore, the reaction of *p*-nitrophenol, like that of $(CF_3)_3COH$, with hydrides **1**—**3** in THF gives, according to IR spectroscopy, results in a DHB and in proton transfer with generation of $(\eta^2\text{-}H_2)$-complexes.[7] For *p*-nitrophenol and *p*-nitrophenolate, the UV-Vis bands appear at λ_{max} = 300—320 and 406—426 nm, respectively (the exact λ_{max} values are strictly dependent on the solvent and temperature).[8,10]

Low-temperature (190 K) spectra of the Ru and Os dihydrides in THF showed bands with λ_{max} = 330 nm, logε = 3.9 (**2**) and λ_{max} = 325 nm, logε = 3.7 (**3**). In

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contrast, the iron dihydride **1** gave only a low-intensity shoulder in the visible region belonging to a shorter-wavelength UV band. In the presence of a stoichiometric amount of *p*-nitrophenol, the spectra of hydrides **2** and **3** showed very broad absorption (310—360 nm), which includes the overlapped bands of dihydrogen bonded species **B**, the initial hydrides, and the proton donor **A** (see Scheme 1). The new long-wavelength band appearing at λ_{max} = 394 nm (logε = 4.3) is slightly blue-shifted ($\Delta\lambda_{max}$ = 29 nm) in comparison with that exhibited by the free phenolate anion (λ_{max} = 423 nm, logε = 4.5). A shorter-wavelength absorption compared to the corresponding anion is known[8—10] to be indicative of the formation of ion pairs. Thus the band at 394 nm can be assigned to ion pairs **C** stabilized by a hydrogen bond between the cation containing the (η^2-H$_2$)-ligand and *p*-nitrophenolate anion (Fig. 1). A similar trend has been reported for H-bonded ion pairs involving amines ($\Delta\lambda_{max}$ = 20—30 nm).[8,10] Raising the temperature from 190 to 250 K shifts the equilibrium shown in Scheme 1 to the left. Accordingly, the new band at 394 nm, due to **C**, decreases in intensity, while the bands in the 320—360 nm region (**A** + **B**) become more intense, demonstrating the reversibility of the process.

Further support to the formation of ion pairs of type **C** was obtained by studying the deprotonation of the dihydrogen complex [{P(CH$_2$CH$_2$PPh$_2$)$_3$}Os(H)(η^2-H$_2$)]$^+$BPh$_4^-$ (**4**) with potassium *p*-nitrophenolate in THF in the presence of excess 18-crown-6 at 190 K. Figure 2 shows that the UV band typical of the *p*-nitrophenolate anion (λ_{max} = 423 nm) disappears in the presence of complex **4**. Found in its place is absorption at 394 nm assigned to the ion pairs. The broad absorption characterizing, as shown above, the existence of the **A** + **B** mixture is observed in the 310—340 nm region. An increase in the temperature to 260 K decreased the intensity of the ion-pair band and increased the intensity of the absorption in this region. Therefore, one may conclude that deprotonation of complex **4** involves the formation of ion pairs **C**.

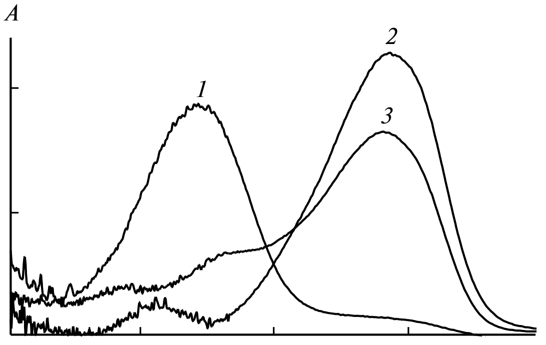

Fig. 1. Electronic spectra of THF solutions containing *p*-nitrophenol (C = 0.001 mol L^{-1}) and the dihydrides [{P(CH$_2$CH$_2$PPh$_2$)$_3$}FeH$_2$] (*1*), [{P(CH$_2$CH$_2$PPh$_2$)$_3$}RuH$_2$] (*2*), and [{P(CH$_2$CH$_2$PPh$_2$)$_3$}OsH$_2$] (*3*) (C = 0.001 mol L^{-1}), after subtracting the respective dihydride absorption band at 190 K.

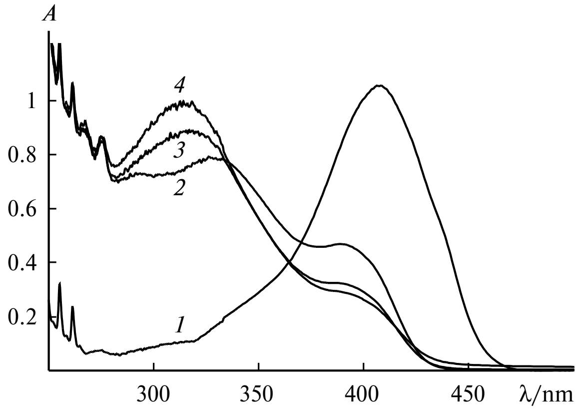

Fig. 2. Electronic spectra of THF solutions containing potassium *p*-nitrophenolate (C = 0.001 mol L^{-1}) with an excess of 18-crown-6 (*1*) and in the presence of [{P(CH$_2$CH$_2$PPh$_2$)$_3$}Os(H)(η^2-H$_2$)]$^+$BPh$_4^-$ (**4**) (C = 0.001 mol L^{-1}) at 200 (*2*), 230 (*3*), and 260 K (*4*).

Analysis of the band intensity at λ_{max} = 394 nm for an equimolar mixture of *p*-nitrophenol and each of the dihydrides **1**—**3** provides valuable information on the extent of proton transfer. This study shows that iron hydride **1** interacts weakly with the acid. Indeed, for iron we observed only a small broadening of the *p*-nitrophenol band and insignificant absorbance in the region of ionic species (λ_{max} = 394 nm) (see Fig. 1, curve *1*). In contrast, high intensity of the band at 394 nm was found in the spectrum containing Ru hydride compared to that for Os hydride (see Fig. 1, curves *2* and *3*). The extents of proton transfer α in percent calculated from the optical densities are 10, 81, and 55 for Fe (**1**), Ru (**2**), and Os (**3**) complexes, respectively. Thus, the propensity of the present metal dihydrides to form ion pairs of type **C** varies aperiodically down the iron triad in the order FeH $\ll$ OsH < RuH. Remarkably, this trend is different from that observed for the proton-acceptor capacity of the hydride ligand in the DHB that steadily increases down the group, FeH < RuH < OsH.[2,7] A similar aperiodic trend (Fe < Os < Ru) in the acidity for some cationic hydrides with η^2-H$_2$-ligands has been previously reported[12,13] and explained in terms of a stronger (shorter) H—H bond in the ruthenium dihydrogen complex as compared to the osmium derivative.

In conclusion, the present work has demonstrated that low-temperature electronic spectroscopy can be an efficient tool to investigate the stepwise protonation of transition metal hydrides yielding ionic H-complexes and the dependence of the extent of protonation of transition metal hydrides on the position of the metal atom in the Periodic Table.

Experimental

Dihydride complexes **1**—**3** and dihydrogen complex **4** were prepared as described previously.[14] Low-temperature UV-Vis measurements were carried out using a Specord M-40 spectrometer using the procedure of low-temperature measurements described for IR spectra.[5,6] The extent of proton transfer was calculated using the formula $[A/(\varepsilon l C_{\text{init}})] \cdot 100\%$, where A and ε are the optical density and the molar extinction coefficient of the band at 394 nm, respectively, C_{init} is the initial concentration of *p*-nitrophenol, l is the cell thickness.

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