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COMMUNICATIONS

Intermolecular Hydrogen Bonding between Neutral Transition Metal Hydrides $(\eta^5\text{-}C_5H_5)M(CO)_3H$ (M = Mo, W) and Bases

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Transition metal hydrides exhibit two modes of reactivity in proton transfer reactions, showing either acid or basic behavior depending on the substrates. During the past decade, it was shown that a hydride ligand could be the proton accepting site in the hydrogen-bonded complex $M-H^{\delta-}\cdots H^{\delta+}X$, whose formation precedes the proton transfer, yielding cationic $M(\eta^2\text{-}H_2)$ complexes.[1] At the same time, many neutral hydrides are known to be strong acids.[2] Therefore, it could be supposed that proton transfer from transition metal hydrides should be preceded by the formation of molecular $MH\cdots B$ hydrogen bonds (where B is a base), as for X−H acids. However, such hydrogen bonds are uncommon.[1,3] The ion molecular $[MH]^+\cdots B$ interaction was found in IR studies (in the ν_{MH} and ν_{PO} regions) of phosphine oxides and $[Cp^*{}_2OsH]^+PF_6^-$ in solution[4] or $[IrH_2(PPh_3)_2L_2]^+BF_4^-$ in the solid state.[5] The changes in IR frequencies revealed were the same as those for classical hydrogen bonds, confirming that the polarization of the metal−hydrogen bonds is $M-H^{\delta+}$. In their classical work, Norton et al. studied the interaction between $HCo(CO)_4$ and a series of nitrogen and oxygen bases, but found no evidence for such a hydrogen bond.[6] Thus, the existence of an *inter*molecular $M-H\cdots B$ hydrogen bond for a *neutral* transition metal hydride in solution is still an unanswered question.[7] Another major question[3] is whether some M−H bonds are polarized $M^{\delta}\cdots H^{\delta+}$ prior to hydrogen bond formation or whether this polarization (repolarization of metal−hydride $M^{\delta+}-H^{\delta-}$ bond) is the result of $M-H\cdots B$ hydrogen bonding.

In this communication, we report spectroscopic and theoretical evidence for the intermolecular hydrogen bond with neutral hydride complex as an acid. For this study, we chose well-known $CpM(CO)_3H$ hydride complexes (M = Mo, W) which are less acidic[2] than $HCo(CO)_4$ studied by Norton et al.[6] In the 2200−1600 cm^{-1} region of IR spectra, they exhibit in solution two strong ν_{CO} bands and weak ν_{MH} bands (see Table 1), which appeared to be sensitive to the presence of organic bases in the solution (Table 1).

Thus the addition of an excess of pyridine (Py) or phosphine oxides ($(n\text{-}C_8H_{17})_3P{=}O$, $((CH_3)_2N)_3P{=}O$) causes the appearance of low frequency shoulders/bands of ν_{CO} and ν_{MH} bands ($\Delta\nu_{CO} = 4-12$ and $\Delta\nu_{MH} = 9-12$ cm^{-1}), while a new low frequency shifted ν_{PO} band of H-bonded $((CH_3)_2N)_3P{=}O$ grows up in the presence the hydride excess ($\Delta\nu_{PO} = 12$ cm^{-1}). The $\Delta\nu_{MH}$ and $\Delta\nu_{PO}$ values are comparable to those observed for ion molecular hydrogen bonds.[4,5] These spectral changes are slightly more pronounced for molybdenum than for tungsten. The H-bonding equilibrium shifts to the right upon the increase of the base/hydride excess (Figure 1) or lowering the temperature (Figure S1).

Similar spectral changes were observed upon the addition of BH_3NEt_3 hydride to the hexane solution of $CpW(CO)_3H$. Low frequency shifts of carbonyl bands (to 2024 and 1934 cm^{-1}) are comparable to those in the presence of pyridine; the changes in the ν_{BH} region are similar to those observed for regular proton donors. Interestingly, the ν_{WH} band undergoes a larger low frequency shift, and a $\nu_{WH\cdots HB}$ band of dihydrogen-bonded adduct appears at 1822 cm^{-1} (Figure 2). This is the first example where dihydrogen bond formation was observed between two neutral hydride complexes.

Table 1. Spectroscopic Characteristics for $CpM(CO)_3H$ Hydrides and Their Hydrogen-Bonded Adducts with Pyridine and $(n\text{-}C_8H_{17})_3PO$ in Hexane at 290 K

	Mo		W	
	ν_{CO}	ν_{MH}	ν_{CO}	ν_{MH}
free hydride	2030 1946	1790	2028 1939	1848
Py	2024 1936	*a*	2024 1932	*a*
$(n\text{-}C_8H_{17})_3PO$	2024 1936	1780	2022 1928	1839

[a] In the presence of Py, the ν_{MH} bands are masked by wide ν_{CO} bands.

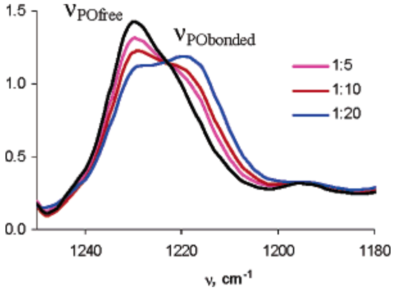

Figure 1. IR spectra of $((CH_3)_2N)_3P{=}O$ (0.01 M) in the presence $CpMo(CO)_3H$. Hexane, 290 K.

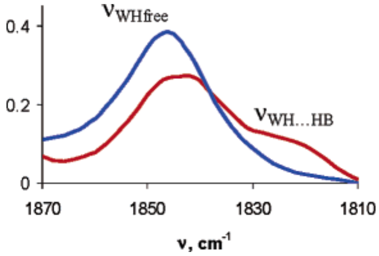

Figure 2. Changes of ν_{WH} band of $CpW(CO)_3H$ (0.05 M) in the presence of H_3BNEt_3 (0.5 M). Hexane, 290 K.

In contrast to bases, no ν_{CO} and ν_{MH} band shift was observed with indole, suggesting the absence of $XH\cdots OC$ or $XH\cdots HM$ hydrogen bonding (X = N, C) with this proton donor or with CH groups of the bases used.

The addition of a large excess of $(n\text{-}C_8H_{17})_3PO$ (0.3 M) to hexane−CH_2Cl_2 (10:1) solution or dissolution of $CpM(CO)_3H$

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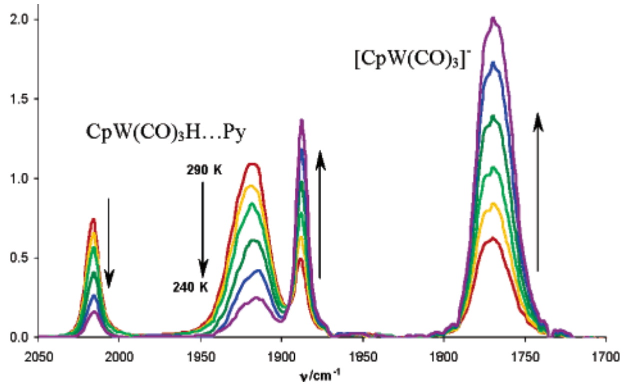

Figure 3. Variable temperature IR spectra in the ν_{CO} region of $CpW(CO)_3H$ (0.005 M) in neat pyridine. Spectra measured between 240 and 290 K with 10 K increments.

Table 2. Optimized Geometrical Parameters (bond distances in angstroms; angles in degrees), Mulliken Charges (*q*), and Stretching Vibration Frequencies (in cm^{-1}) for $CpM(CO)_3H$ Hydrides and Their Hydrogen-Bonded Complexes with Pyridine

	MoH	MoH•Py	WH	WH•Py
M−H	1.724	1.729	1.735	1.738
H•••N		2.648		2.925
M−H•••N		160.6		162.8
q(M)	−0.119	−0.180	−0.073	−0.141
q(H)	0.112	0.200	0.127	0.204
q(N)		−0.380[a]		−0.373[a]
ν_{M-H}	1800	1767 (−33)[b]	1857	1844 (−13)[b]
ν^1_{CO} (sym A′)	1996	1987 (−9)[b]	1995	1989 (−6)[b]
ν^2_{CO} (asym A″)	1924	1912 (−12)[b]	1919	1912 (−7)[b]
ν^3_{CO} (asym A′)	1923	1907 (−16)[b]	1918	1904 (−14)[b]

[a] *q*(N) of free pyridine is −0.368. [b] In parentheses, $\Delta\nu = \nu_{adduct} - \nu_{free}$.

complexes in neat pyridine causes partial proton transfer, as is evident from the appearance of two ν_{CO} bands of $[CpM(CO)_3]^-$ anions at 1895 and 1776 cm^{-1} for Mo, and 1888 and 1770 cm^{-1} for W. The ν_{CO} bands of the anions reversibly grow up with temperature decrease (Figure 2), indicating the shift of the proton transfer equilibrium (eq 1) to the right upon cooling. Quantitative analysis of the intensity changes in Figure 3 gives thermodynamic parameters for the proton transfer step: $\Delta H = -7.0$ kcal mol^{-1}, $\Delta S = -26.1$ e.u.

$$[M]{-}H + B \rightleftarrows [M]{-}H{\cdots}B \xrightleftharpoons{\text{excess B}} [M]^- + [H(B)_n]^+ \quad (1)$$

$$[M] = CpM(CO)_3,\ B = R_3PO,\ Py$$

To shed more light on this rare type of hydrogen bonding, the DFT calculations were performed[8] for the $CpM(CO)_3H$ hydrides (M = Mo, W) and their adducts with pyridine. The main geometrical parameters of free hydrides and their hydrogen-bonded complexes obtained are summarized in the Table 2 together with relevant stretching vibration frequencies and Mulliken charges of atoms involved in the interaction (MH, N). The hydrogen-bonded adducts have rather short hydrogen−nitrogen contacts, comparable to the CH•••N distances in hydrogen-bonded adducts of similar strength[9] and close to the linear arrangement of the M−H•••N moiety. The deviation of M−H•••N angle from 180° might be caused by additional attraction between the CH groups of pyridine adjacent to nitrogen and metal-bound carbonyls. The M−H bonds elongate upon hydrogen bond formation (see Table 2), as expected. All changes are more pronounced for molybdenum than for the tungsten analogue. The interaction energies of both adducts are typical for weak hydrogen bonds,[10] but again the values obtained reflect stronger interaction in the case of molybdenum hydride ($\Delta E_{ZPE} = -2.25$ kcal mol^{-1}) than of tungsten ($\Delta E_{ZPE} = -2.05$ kcal mol^{-1}).

Analysis of charge distributions in free hydrides (Mulliken charges) and their variation after hydrogen bond formation shows that polarization of the metal hydrogen bond in free hydrides is already $M^{\delta-}{-}H^{\delta+}$ (Table 2). Upon the formation of the hydrogen-bonded complexes, the positive charge of the metal-bound hydrogen atom increases by 0.088 and 0.077 units for MoH and WH, respectively, while the charge of the metal atom itself becomes more negative by ca. −0.06 units. Hydrogen bonding leads also to the increase of electron density on the nitrogen atom of pyridine. In addition, there is a small positive overlap population of H•••N bonds of 0.103 and 0.074 units for molybdenum and tungsten hydride, respectively. All these electronic changes, although relatively small in magnitude, are comparable to those established for conventional hydrogen bond donors and acceptors.[11]

Finally, frequency calculations confirm the experimental IR observations. The ν_{CO} and ν_{MH} frequencies calculated for free hydrides are in good agreement with the experimental values. Two lower frequency ν_{CO} stretching modes (ν^2_{CO} and ν^3_{CO}) have very close frequencies, and consequently only one band was observed in the spectra in solution. All bands of hydrogen-bonded adducts appear at lower frequencies, the band shift values $\Delta\nu$ being larger for molybdenum than for tungsten (Table 2).

In conclusion, the experimental and theoretical results show for the first time the formation of intermolecular hydrogen bonds between the neutral transition metal hydrides $CpM(CO)_3H$ as proton donors and bases which precede the hydride deprotonation. Intermolecular dihydrogen bond (H•••H) was found between two neutral hydride complexes using H_3BNEt_3 as a base. Further studies of the nature of the MH•••B interaction as well as of thermodynamics of the M−H•••B bond formation and subsequent proton transfer are in progress.

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Supporting Information Available: Experimental and computational details, drawings, and tables of the optimized geometries for the calculated species. This material is available free of charge via Internet at http://pubs.acs.org.

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