

Metal Hydrides Form Halogen Bonds: Measurement of Energetics of Binding

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Supporting Information

ABSTRACT: The formation of halogen bonds from iodopentafluorobenzene and 1-iodoperfluorohexane to a series of bis(η^5 -cyclopentadienyl)metal hydrides (Cp_2TaH_3 , **1**; Cp_2MH_2 , $M = \text{Mo}$, **2**, $M = \text{W}$, **3**; Cp_2ReH , **4**; $\text{Cp}_2\text{Ta}(\text{H})\text{CO}$, **5**; $\text{Cp} = \eta^5$ -cyclopentadienyl) is demonstrated by ^1H NMR spectroscopy. Interaction enthalpies and entropies for complex **1** with $\text{C}_6\text{F}_5\text{I}$ and $\text{C}_6\text{F}_{13}\text{I}$ are reported ($\Delta H^\circ = -10.9 \pm 0.4$ and -11.8 ± 0.3 kJ/mol; $\Delta S^\circ = -38 \pm 2$ and -34 ± 2 J/(mol·K), respectively) and found to be stronger than those for **1** with the hydrogen-bond donor indole ($\Delta H^\circ = -7.3 \pm 0.1$ kJ/mol, $\Delta S^\circ = -24 \pm 1$ J/(mol·K)). For the more reactive complexes **2–5**, measurements are limited to determination of their low-temperature (212 K) association constants with $\text{C}_6\text{F}_5\text{I}$ as 2.9 ± 0.2 , 2.5 ± 0.1 , <1.5 , and $12.5 \pm 0.3 \text{ M}^{-1}$, respectively.

Many parallels exist between hydrogen bonding and halogen bonding. The discovery of hydrogen bonding to metal hydrides was a milestone in understanding intermolecular interactions.¹ We now address the question of the existence of halogen bonds to metal hydrides. Over the past decade, the study of halogen bonding² has undergone dramatic development, and such highly directional intermolecular interactions, in which a Lewis acidic, covalently bound halogen interacts with a Lewis basic site, have been found to be significant in fields such as molecular recognition, supramolecular assembly, materials chemistry, and structural biology.³ Halogen bonding is most commonly observed for the heavier halogen iodine, where the lower electronegativity and higher polarizability give rise to a significant electropositive site on the halogen. This Lewis acidic region, termed the σ -hole, is enhanced by the presence of an electron-withdrawing group bound to iodine; e.g., $\text{C}_6\text{F}_5\text{I}$ is a better halogen-bond donor than $\text{C}_6\text{H}_5\text{I}$.

Only recently has an evaluation of the relative strength of halogen-bond interactions and a quantification of binding to a range of organic substrates been undertaken by the groups of Laurence, Hunter, and Taylor, among others.⁴ However, thermodynamic data for these interactions with metal complexes are restricted to metal monofluoride complexes, despite the widespread use of metal–organic building blocks in the construction of halogen-bonded supramolecular architectures.⁵ Previous experimental studies by our group have focused upon the energetics of hydrogen and halogen bonding to group 10 fluoride complexes, indicating that the enthalpy of binding to

iodopentafluorobenzene ($\text{C}_6\text{F}_5\text{I}$) in toluene ranges from -16 to -25 kJ/mol and revealing that the magnitude of the enthalpy increases as $\text{Ni} < \text{Pd} < \text{Pt}$.⁶ Comparison of the strength of the interaction of $\text{C}_6\text{F}_5\text{I}$ and indole with a nickel fluoride shows that the halogen bond is weaker than the hydrogen bond.

Metal halides are well-established as good acceptors of both hydrogen bonds⁷ and halogen bonds.⁸ Although many other ligands participate in hydrogen bonding,⁹ corresponding examples of ligands acting as halogen-bond acceptors are less common.^{2b,10} Metal hydrides, pervasive species in organometallic catalysis, are well established as hydrogen-bond acceptors, and this “dihydrogen-bonding” state can be considered as an intermediate in protonation and formation of dihydrogen complexes.¹ In contrast, the potential of metal hydrides to act as acceptors for halogen bonds is unexplored, despite recent theoretical investigations.^{10a} Here we quantify the strengths of halogen bonds to some groups 5 and 6 bis(η^5 -cyclopentadienyl)metal hydrides and compare them to the strength of interaction of the hydrogen-bond donor, indole.

Preliminary tests of the early transition metal hydrides and those of iron and ruthenium confirmed our suspicions that the early metals, i.e., those metals that impart significant electron density to their hydride ligands, would be most suitable for further study. The selection of metal hydride complexes is based, in addition, on their solubility in nonpolar solvents at low temperature and the requirement for limited reactivity toward the halogen-bond donors. The chemical properties and reactivity of the bis(η^5 -cyclopentadienyl)metal hydrides of groups 5 and 6 are well-established, with the Lewis basicity of their hydrides arising by virtue of the electropositivity of the metal and for **2–5** by the lone pair of electrons of the metal.^{11,12} NMR spectroscopic titrations were undertaken using a series of early transition metal hydrides in combination with two established halogen-bond donors. Interaction with the extensively studied hydrogen-bond donor indole was measured as a reference (Chart 1); indole is a H-bond donor but not an acceptor and is not a competitive ligand unless deprotonated.¹³

Bis(η^5 -cyclopentadienyl)tantalum trihydride (Cp_2TaH_3 , **1**) fulfilled our requirements as a test molecule; additionally, it contains two different hydride environments that lie in a plane giving a “hydridic front”. Initial measurements of the ^1H NMR spectroscopic chemical shifts for Cp_2TaH_3 as the host, upon increasing concentration of guest $\text{C}_6\text{F}_5\text{I}$ at 279 K, revealed an upfield shift of both hydride resonances, with a greater shift for

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Chart 1. Hydride Complexes, Hydrogen-Bond Donors, and Halogen-Bond Donors

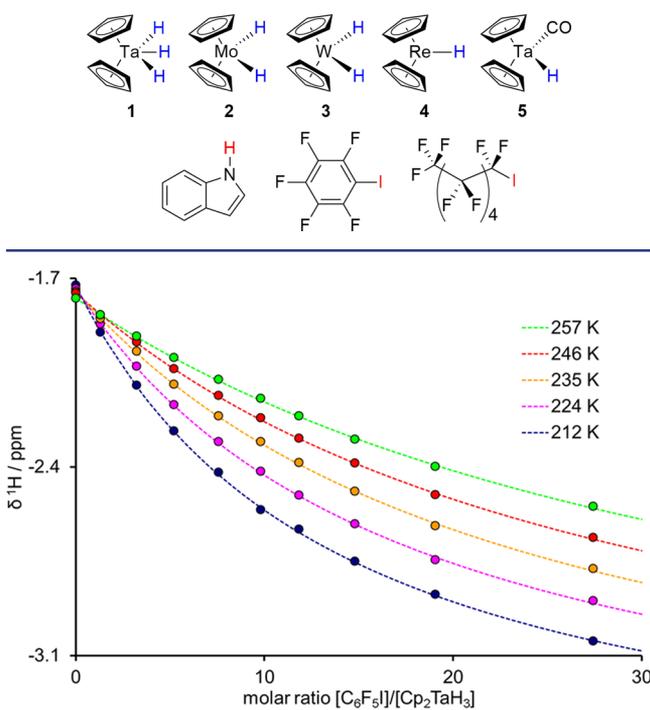
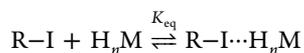


Figure 1. Titration curves at different temperatures for C_6F_5I and Cp_2TaH_3 , showing $\delta(^1H)$ vs $[C_6F_5I]/[Cp_2TaH_3]$ for the triplet signal of the hydride ligand. $[Cp_2TaH_3] = 17 \text{ mmol/dm}^3$. Circles, experimental points; broken lines, best fit to a 1:1 binding isotherm.

the triplet signal (H_{central} triplet, $\Delta\delta 0.39$; H_{lateral} doublet, $\Delta\delta 0.07$ ppm with 15.4 equiv of C_6F_5I , where $\Delta\delta$ is the observed change in chemical shift). A plot of the chemical shift change of the triplet resonance versus the ratio of $[C_6F_5I]/[Cp_2TaH_3]$ gave a curve indicative of binding. We attribute this behavior to the formation of an adduct with the halogen-bond donor predominantly through interaction with the H_{central} (i.e., $C-I\cdots H-Ta$). Cp_2TaH_3 was found to be sufficiently stable toward C_6F_5I at ambient temperature over several hours, permitting data to be collected at a range of temperatures (Figure 1).

Surprisingly, further studies of Cp_2TaH_3 revealed that, upon addition of similar ratios of a perfluoroalkyl iodide donor (1-iodoperfluorohexane, $C_6F_{13}I$), the triplet resonance progresses upfield of the doublet resonance. At a ratio of 8.4 equiv at 224 K (Figure 2), the two signals coalesce, and second-order coupling is observed at ratios near to signal coalescence. In contrast, introduction of indole as a hydrogen-bond donor results in a far less drastic change in chemical shift of the triplet signal and perturbs the doublet environment only slightly (see Figure S12). NMR titrations of Cp_2TaH_3 with indole and $C_6F_{13}I$ were conducted at a range of temperatures, although the latter study was limited to measurements below 250 K to avoid iodination. Equilibrium constants were determined by fitting the NMR spectroscopic titration data for the variation in hydride chemical shift with changing guest concentration to a 1:1 host-to-guest model. Van't Hoff plots yielded enthalpy and entropy values.¹⁴



The equilibrium constant (K_{eq}) for interaction of **1** with $C_6F_{13}I$ at 212 K is $14.2 \pm 0.2 \text{ M}^{-1}$, considerably higher than its value with

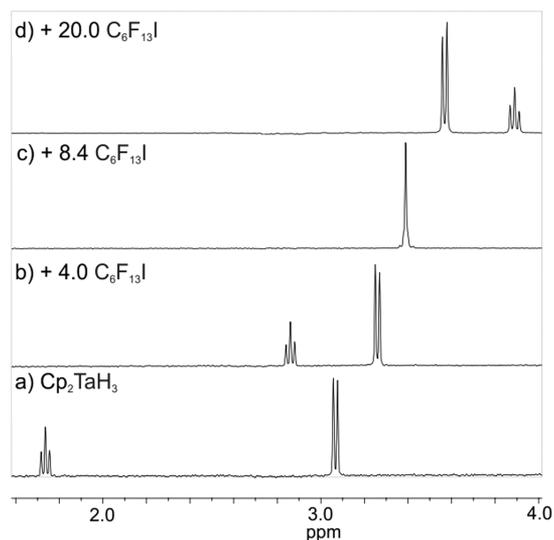


Figure 2. Stack plot of the hydride region of the 1H NMR spectra of Cp_2TaH_3 at 224 K with increasing equivalents of $C_6F_{13}I$ in toluene- d_8 .

Table 1. Summary of Thermodynamic Parameters^a

compound	Lewis acid	ΔH° , kJ/mol	ΔS° , J/(mol·K)	K_{212} , M^{-1}
Cp_2TaH_3 (1)	C_6F_5I	-10.9 ± 0.4	-38 ± 2	4.6 ± 0.1
	$C_6F_{13}I$	-11.8 ± 0.3	-34 ± 2	14.2 ± 0.2
	indole	-7.3 ± 0.1	-24 ± 1	3.6 ± 0.1^b
Cp_2MoH_2 (2)	C_6F_5I			2.9 ± 0.2
	C_6F_5I			2.5 ± 0.1
Cp_2WH_2 (3)	indole	-7.5 ± 0.1	-28 ± 1	2.5 ± 0.1
	C_6F_5I			< 1.5
$Cp_2Ta(H)CO$ (5)	C_6F_5I			12.5 ± 0.3

^aErrors at the 95% confidence level. Toluene- d_8 /toluene- h_8 solvent.

^bRecorded at 211 K. ^cOnly low-temperature association constants were measured due to the reactivity toward C_6F_5I .

C_6F_5I , $4.6 \pm 0.1 \text{ M}^{-1}$, and consistent with measurements by Taylor for halogen-bond donors with nitrogen bases.¹⁵ The enthalpy for the interaction of **1** with $C_6F_{13}I$, $-11.8 \pm 0.3 \text{ kJ/mol}$, is marginally stronger than that with C_6F_5I ($-10.9 \pm 0.4 \text{ kJ/mol}$) (Table 1). For indole, the enthalpy is notably weaker, at $-7.3 \pm 0.1 \text{ kJ/mol}$, than for C_6F_5I , in contrast to the opposite trend observed for a nickel fluoride.^{6a}

Near-ambient temperature measurements with Cp_2MoH_2 (**2**), Cp_2WH_2 (**3**), and $Cp_2Ta(H)CO$ (**5**) were precluded by iodination.¹⁶ The rate of iodination varies appreciably with the complex; the most reactive complex, $Cp_2Ta(H)CO$, reacts with C_6F_5I nearly instantaneously at 298 K. The high reactivity of **2**, **3**, and **5** toward C_6F_5I limited us to single temperature measurements of their association constants at 212 K. The association constants recorded at this temperature for binding of C_6F_5I diminish with decreasing basicity of the hydride (Table 1, inferred from the increasing electronegativity, χ , of the metal: Ta, 1.5; Mo, 2.16; W, 2.36).^{17,18} In an attempt to expand our library of halogen-bonding hydrides, we conducted an analogous NMR titration with Cp_2ReH (**4**), isoelectronic to Cp_2TaH_3 and Cp_2WH_2 . Titration of **4** against C_6F_5I did indicate the presence of an interaction, although it was too weak to determine reliably; our measurements gave a value of $K_{\text{eq}} < 1.5 \text{ M}^{-1}$ (Figure S11).

Of the hydrides investigated, **5** was found to be a marginally stronger halogen-bond acceptor than complexes **1**–**3**, but we were interested to determine the extent of involvement of the

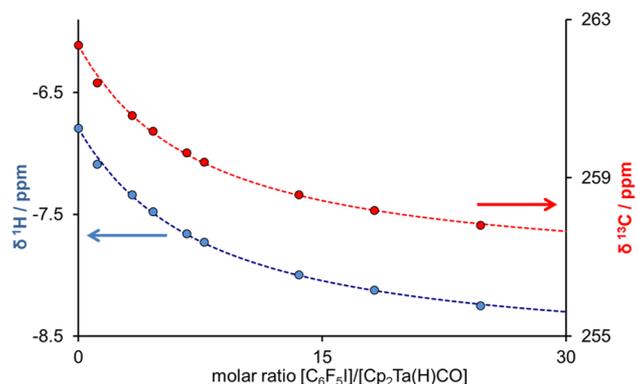


Figure 3. Titration curves at 212 K for C_6F_5I and $Cp_2Ta(H)^{13}CO$ showing $\delta(^1H)$ (blue) and $\delta(^{13}C)$ (red) vs $[C_6F_5I]/[Cp_2Ta(H)^{13}CO]$. $[Cp_2Ta(H)^{13}CO] = 11 \text{ mmol/dm}^3$. Circles, experimental points; broken lines, best fit of each data set to independent 1:1 binding isotherms.

CO ligand. Therefore, a complementary study was undertaken of isotopically enriched **5**, $Cp_2Ta(H)^{13}CO$, monitoring the carbonyl resonance in the $^{13}C\{^1H\}$ NMR spectrum and the hydride resonance in the 1H NMR spectrum simultaneously as C_6F_5I was added. Titration of $Cp_2Ta(H)^{13}CO$ against C_6F_5I at 212 K revealed a significant upfield shift of the ^{13}C resonance (Figure 3) from 262.4 to 257.8 ppm (24.7 equiv). The fitted association constant of this observed ^{13}C binding curve is 13.1 M^{-1} and corresponds well with the value of 12.5 M^{-1} obtained from fitting of the hydride signal on the same sample, suggesting that both are representative of the same mode of interaction with **5**.

In contrast to the upfield movement of NMR chemical shifts observed for **5**, the complex $(\eta^5-C_5Me_5)Mo(PMe_3)_2(CO)H$ exhibits downfield shifts for both 1H and ^{13}C NMR resonances upon introduction of fluorinated alcohols, with the site of interaction identified to be the carbonyl, not the hydride from IR spectra.¹⁹ Previous studies upon $Cp_2M(H)CO$ ($M = Nb, Ta$) have demonstrated the preference of Lewis acids such as AlR_3 ($R = Me, Et$) to complex the hydridic site, whereas binding to the carbonyl oxygen is only observed for metallocenes in which steric shielding prevents access to the hydride, such as $(\eta^5-C_5Me_5)_2Ta(H)CO$.^{20,21} The observation that both 1H and ^{13}C NMR resonances move upfield on titration of $Cp_2Ta(H)CO$ against C_6F_5I supports interaction with the hydride.²²

For Cp_2TaH_3 (**1**) the only sites of basicity are the hydrides, but for complexes **2–5** a metal-based lone pair exists as a possible contributor to the binding of the weak Lewis acids. The group 6 Cp_2MH_2 hydrides, however, bind more weakly to C_6F_5I than the group 5 hydrides, and Cp_2ReH , possessing two metal-based lone pairs, shows the weakest binding of all.^{11b}

DFT calculations were undertaken on **1**, **3**, and **5** to distinguish the possible binding modes of C_6F_5I toward the metallocene hydrides.^{23–25} The geometries and energies of the separate components and of the adducts were calculated and compared to one another. The BHandHLYP functional was employed because of its success in modeling non-covalent interactions.^{6b,26} Two geometries were envisaged for interaction of **1** with C_6F_5I : a bifurcated mode, where iodine interacts with both the central and a more distant lateral hydride, and a “side-on” mode, where iodine binds solely to a lateral hydride. Such interaction modes would resemble those geometries observed for metal halides.²⁷ Our calculations converged for a bifurcated interaction involving the central hydride ($I\cdots H$ 2.762 Å, $C-I\cdots H$ 173.5°) and one of the two lateral hydrides ($I\cdots H$ 3.324 Å, $C-I\cdots H$ 152.4°) with an

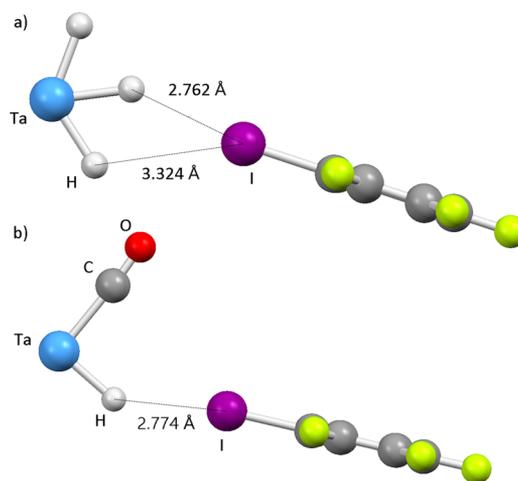


Figure 4. Optimized minima for adducts of C_6F_5I with (a) Cp_2TaH_3 (**1**) and (b) $Cp_2Ta(H)CO$ (**5**) ($I\cdots C$ 4.094 Å, $I\cdots O$ 4.477 Å). Cyclopentadienyl rings omitted for clarity.

interaction energy of -13.4 kJ/mol (Figure 4a). No minimum was located for “side-on” binding. The calculated bifurcated geometry correlates well with the experimental observation that the central hydride undergoes a greater chemical shift change relative to the lateral hydride upon introduction of C_6F_5I .²⁸ All the NMR data are obtained in the fast exchange limit, so we would not expect to observe any inequivalence of the hydrides through halogen bonding. Previous studies by Bakhmutova et al. of $O-H\cdots H-Nb$ hydrogen bonds involving Cp_2NbH_3 and fluorinated alcohols predicted a bifurcated interaction with a shorter distance to the central than to the lateral hydrides.^{1e}

Exploration of bifurcated and side-on geometries for Cp_2WH_2 (**3**) gave minima for both with calculated binding energies of -13.4 and -12.1 kJ/mol , respectively. Assuming that the interactions are predominantly electrostatic, an alternative approach to modeling the behavior of the adducts is to calculate the electrostatic potential of the metal hydrides alone. We found that the electrostatic potential in the MH_n plane of the **1** and **3** varies very little across the hydridic front when probed at a typical $H\cdots I$ distance (see Figures S21–S23). Thus, this method is consistent with the small differences in interaction energies for the different binding geometries examined for **3** + C_6F_5I .

Calculations on $Cp_2Ta(H)CO$ (**5**) showed an energetic preference for binding to the hydride position rather than the carbonyl, in keeping with experiment (calculated to hydride, -14.3 kJ/mol ; to carbonyl, -8.3 kJ/mol). One could also envisage iodine engaging in a bifurcated interaction with **5**, functioning as an electrophile to H through the σ -hole and a nucleophile to the π^* of CO via an iodine lone pair,²⁹ but a minimum for this geometry was not found. Moreover, in optimized geometries of adducts bound through hydride, the $I\cdots C$ and $I\cdots O$ distances exceed the sum of the van der Waals radii, ruling out any significant synergistic binding (Figure 4b).

We have demonstrated for the first time that early transition metal hydrides are capable of acting as halogen-bond acceptors. The equilibrium constants for interaction with C_6F_5I at 212 K increase in the order $Cp_2ReH < Cp_2WH_2 \sim Cp_2MoH_2 < Cp_2TaH_3 < Cp_2Ta(H)CO$. The calculations model the enthalpy of interaction of Cp_2TaH_3 with C_6F_5I successfully (expt -10.9 ± 0.4 , calcd -13.4 kJ/mol), but the interaction energies are too small to model the trends with confidence. There is a close analogy between dihydrogen bonding and halogen bonding to

hydrides. Surprisingly, the interaction energy of **1** with C_6F_5I is greater than that with indole, in contrast with the behavior of nickel fluorides (ΔH° for indole $N-H\cdots F-Ni$, -23.4 ± 0.2 ; for $C_6F_5I\cdots F-Ni$, -16 ± 1 kJ/mol).^{6a} Dihydrogen bonding has proved to be significant in understanding the reactivity of metal hydrides,¹ and we anticipate that the same will be true of halogen bonding.

■ ASSOCIATED CONTENT

● Supporting Information

Further spectroscopic and computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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- (23) Calculations were performed by use of the Gaussian 09 series of programs²⁴ at the DFT level using the BHandHLYP functional. This functional has been shown to provide accurate energetics for non-covalently bonded systems.²⁶ The SDD effective core potential and associated basis sets were used for Ta, W, and I. The 6-31G** basis set was used for C, H, F, and O, and diffuse functions were added to O and the hydrides. All the geometries were optimized without restraint, and we used an ultrafine grid together with tight optimization criteria. Interaction enthalpies were corrected for basis set superposition error using the counterpoise method.²⁵
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- (29) An asymmetric approach of the iodine lone pair predominantly toward the oxygen-based lobe of the $CO\pi^*$ would be symmetry allowed and would give a positive net bonding contribution to the interaction.