Metal hydrides form halogen bonds: measurement of energetics of binding

Dan A. Smith,† Lee Brammer,*‡ Christopher A. Hunter*‡ and Robin N. Perutz*†

†Department of Chemistry, University of York, Heslington, York, YO10 5DD, U.K.
‡Department of Chemistry, University of Sheffield, Sheffield, S3 7HF, U.K.

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NMR spectroscopic measurements

General procedures

All preparations were performed under argon using glove box or Schlenk line techniques. Solvents were dried and distilled over sodium and degassed prior to use. C₆F₅I and C₆F₁₃I were degassed and dried on 3Å molecular sieves. All chemicals and reagents were purchased from Aldrich. NMR spectra were collected on a Bruker AMX 500 MHz spectrometer. Complexes 1-5 were synthesised by known procedures or taken from laboratory stock.¹ The temperature of the NMR spectrometer was calibrated by using established methods.²

NMR data for 5, Cp₂Ta(H)¹³CO

¹H NMR (C₆D₅CD₃): δ 4.45 (10H, s, CH), −6.91 (1H, d, JCH 5.6 Hz, TaH). ¹³C{¹H} NMR (C₆D₅CD₃): δ 261.3 (s), 82.5 (s).

Standard method for titrations

Stock solutions were prepared by recording the masses of host, guest and the solvent added. To Young’s NMR tap tubes in a glove box were added approximately 400 μL of host stock solution and the exact mass recorded to allow a determination of the number of moles of host in the sample. Similarly the guest was added by syringe and the mass of the addition recorded. To standardise the volume of the samples solvent was added to give a volume of 600 μL. For the measurement the samples were kept in a cold bath at the approximate temperature of the spectrometer and allowed two minutes to equilibrate after insertion.

Additional methodology adopted for measuring highly reactive host-guest systems

Introduction of C₆F₅I into a solution of Cp₂Ta(H)CO at RT resulted in immediate decomposition with no hydride resonances apparent by ¹H NMR spectroscopy and therefore the following procedure was used to prepare samples for low temperature (212 K) experiments. To a Young’s tap NMR tube was added approximately 400 μL of host solution and the tube was weighed accurately. An additional volume of toluene was added so that upon addition of guest the volume

¹ (a) Wilkinson, G.; Birmingham, J. M. J. Am. Chem. Soc. 1955, 77, 3421; (b) Green, M. L. H.; McCleverty, J. A.; Pratt, L.; Wilkinson, G. J. Chem. Soc. 1961, 4854; (c) Tebbe, F. N.; Parshall, G. W. J. Am. Chem. Soc. 1971, 95, 5412; (d) Baynham, R. F. G.; Chetwynd-Talbot, J.; Grebenik, P.; Perutz, R. N.; Powell, M. H. A. J. Organomet Chem. 1985, 284, 229.
² Ammann, C.; Meier, P.; Merbach, A. E. J. Magn. Reson. 1982, 46, 319.
in all tubes totalled 600 μL. The mass of the sealed tube was then recorded and removed from the glove box. The tube was placed into a Schlenk-line adapter possessing both an inlet for inert gas and an open top to allow removal of the Young’s cap. After cooling the samples to -78 °C the guest solution was introduced by removal of the Young’s cap under a strong flow of argon and injection by microsyringe. In all cases the samples were held below -50 °C and the NMR experiments conducted within an hour of sample preparation. During the titration the tubes were inverted before insertion into the NMR machine to ensure mixing and checked for solubility of both host and guest components. After the measurement the total mass of the tube was recorded and from this subtracted the mass of the tube prior to guest addition therefore allowing the mass of guest added to be determined retrospectively. With these precautions only small quantities (1-2%) of decomposition were observed for 2, 3 and 5 in the NMR spectra by the presence of another cyclopentadienyl resonance. Titration samples of 4 were prepared analogously; however a greater degree of iodination of the metal hydride was observed (~10%) and consequently this was accounted for in the fitting analysis.

Composition of stock solutions

Table S1: Composition of stock solutions used for the preparation of samples for halogen and hydrogen bonding measurements by NMR spectroscopy.

| System studied       | Metal hydride (host) stock solution | Dilute Guest stock solution | Concentrated Guest stock solution |
|----------------------|-------------------------------------|----------------------------|----------------------------------|
|                      | Metal hydride / bond donor          | m (MH) / mg                | m (solv) / mg                   | m (Guest) / mg                   | m (solv) / mg                   |
| Cp2TaH3 / C6F5I      |                                     | 41.1                       | 5531.8                          | 103.7                            | 635.8                           | 417.3                           | 328.8                           |
| Cp2TaH3 / C6F13I     |                                     | 42.3                       | 5257.8                          | 311                              | 1540.8                          | 500                             | 0                               |
| Cp2TaH3 / Indole     |                                     | 52                         | 6405                            | 61                               | 605                             | 609                             | 812                             |
| Cp2Ta(H)13CO / C6F5I |                                     | 20.6                       | 3164.7                          | 170.2                            | 669                             | 170.2                           | 669                             |
| Cp2MoH2 / C6F5I      |                                     | 42                         | 6307                            | 227                              | 503                             | 500                             | 0                               |
| Cp2WH2 / C6F5I       |                                     | 45.5                       | 5528.5                          | 126.8                            | 940.5                           | 399.5                           | 308.6                           |
| Cp2WH2 / Indole      |                                     | 49.8                       | 5160.8                          | 59                               | 603.8                           | 406.2                           | 842.1                           |
| Cp2ReH / C6F5        |                                     | 29.5                       | 2714.6                          | 0                                | 0                               | 500                             | 0                               |

a 100% toluene-d₈, b 33% toluene-d₈ / 67% toluene-h₈, c 50% toluene-d₈ / 50% toluene-h₈
Fitting of titration curves

The system involves the formation of the 1:1 adduct between the guest and the respective metal hydride, which takes place by R–I···H–M halogen bonding or R–H···H–M hydrogen bonding. In the scheme X-R is either a halogen or a hydrogen bond donor.

\[ R-I + H_nM \xrightleftharpoons{K_{eq}} \xrightarrow{R-I\cdots H_nM} \]

There are two parameters to be fitted: the equilibrium constant $K$ and the downfield shift from the signal of free metal hydride for the coordinated hydride of the adduct, $\Delta \delta_H$. The two parameters can be fitted for the whole range of temperatures without any restraints by using a Microsoft Excel macro programmed by Professor Christopher Hunter (University of Sheffield). $\Delta H^0$ and $\Delta S^0$ were determined from the van’t Hoff plots of the equilibrium constants by linear regression.
Titration curves and van’t Hoff plots

Figure S1: Fit of the titration curves at different temperatures, showing observed values for $\delta H$ vs. ratio of molar concentrations of $\text{C}_6\text{F}_5\text{I}$ and $\text{Cp}_2\text{TaH}_3$, (concentration of $\text{Cp}_2\text{TaH}_3$ 17 mmol dm$^{-3}$).

Figure S2: van’t Hoff plot of the equilibrium constants from the NMR titration of $\text{C}_6\text{F}_5\text{I}$ and $\text{Cp}_2\text{TaH}_3$. 

$\Delta H^\circ = -10.9(4)$ kJ mol$^{-1}$
$\Delta S^\circ = -38(2)$ J mol$^{-1}$K$^{-1}$
$R^2 = 0.997$
Figure S3: Fit of the titration curves at different temperatures, showing observed values for $\delta H$ vs. ratio of molar concentrations of $\text{C}_6\text{F}_{13}\text{I}$ and $\text{Cp}_2\text{TaH}_3$, (concentration of $\text{Cp}_2\text{TaH}_3$ 17 mmol dm$^{-3}$).

Figure S4: van’t Hoff plot of the equilibrium constants from the NMR titration of $\text{C}_6\text{F}_{13}\text{I}$ and $\text{Cp}_2\text{TaH}_3$. 

\[
\Delta H^\circ = -11.8(3) \text{ kJ mol}^{-1} \\
\Delta S^\circ = -34(2) \text{ J mol}^{-1} \text{ K}^{-1} \\
K^\circ = 0.999
\]
Figure S5: Fit of the titration curves at different temperatures, showing observed values for δH vs. ratio of molar concentrations of indole and Cp₂TaH₃, (concentration of Cp₂TaH₃ 20 mmol dm⁻³).

Figure S6: van’t Hoff plot of the equilibrium constants from the NMR titration of indole and Cp₂TaH₃.
Figure S7: Fit of the titration curves at different temperatures, showing observed values for δH vs. ratio of molar concentrations of indole and Cp₂WH₂, (concentration of Cp₂WH₂ 23 mmol dm⁻³).

Figure S8: van’t Hoff plot of the equilibrium constants from the NMR titration of indole and Cp₂WH₂.
Figure S9: Fit of the titration curve at a single temperature, showing observed values for $\delta H$ vs. ratio of molar concentrations of $\text{C}_6\text{F}_5\text{I}$ and $\text{Cp}_2\text{WH}_2$ (concentration of $\text{Cp}_2\text{WH}_2$ 17 mmol dm$^{-3}$).

Figure S10: Fit of the titration curve at a single temperature, showing observed values for $\delta H$ vs. ratio of molar concentrations of $\text{C}_6\text{F}_5\text{I}$ and $\text{Cp}_2\text{MoH}_2$, (concentration of $\text{Cp}_2\text{MoH}_2$ 17 mmol dm$^{-3}$).
Figure S11: Fit of the titration curve at 212 K, showing observed values for δH vs. ratio of molar concentrations of C₆F₅I and Cp₂ReH, (concentration of Cp₂ReH 32 mmol dm⁻³).

Cp₂TaH₃ with 13.7 equivs of indole

Cp₂TaH₃ with 9.4 equivs of indole

Cp₂TaH₃ with 6.9 equivs of indole

Cp₂TaH₃ with 4.7 equivs of indole

Cp₂TaH₃ with 3.1 equivs of indole

Cp₂TaH₃ with 1.6 equivs of indole

Cp₂TaH₃

Figure S12: Stack plot of the hydride region of the ¹H NMR spectra of Cp₂TaH₃ at 212 K with increasing concentration of indole in toluene-d8.
Interaction of $\text{Cp}_2\text{Ta(H)}^{13}\text{CO}$ with AlMe$_3$

IR and $^1\text{H}$ NMR spectra for hydride bound adducts of the type $\text{Cp}(\eta^5\text{-C}_5\text{R}_5)\text{M(H)}\text{CO-AlEt}_3$ ($R = H, M = \text{Nb}; R = \text{Me}, M = \text{Ta}$) are reported in the literature without $^{13}\text{C}$ NMR spectra. Therefore, to complete the analysis of interaction of $\text{Cp}_2\text{Ta(H)}\text{CO}$ with strong Lewis acids we recorded the $^{13}\text{C}$ NMR spectra of isotopically labelled $\text{Cp}_2\text{Ta(H)}^{13}\text{CO}$ as a function of AlMe$_3$ addition, showing that the reported upfield movement of the $^1\text{H}$ resonance is accompanied by a upfield shift of the $^{13}\text{C}$ resonance, see below.

![Figure S13](image)

*Figure S13:* Plot of observed values for $\delta$H and $\delta$C vs. ratio of molar concentrations of AlMe$_3$ and $\text{Cp}_2\text{Ta(H)}^{13}\text{CO}$ at 298 K.

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3 (a) Tebbe, F. N. *J. Am. Chem. Soc.* 1973, 95, 5412. (b) McDade, C.; Gibson, V. C.; Santarsiero, B. D.; Bercaw, J. E. *Organometallics* 1988, 7, 1.
Calculations

Calculations were performed by use of the Gaussian 09 series of programs\(^4\) at the DFT level using the BHandHLYP functional. This functional has been shown to provide accurate energetics for non-covalently bonded systems.\(^5\) The SDD effective core potential and associated basis sets was 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 used an ultrafine grid together with tight optimization criteria. Energies and geometries were optimised for the separate components and for the adducts. Electrostatic potentials were plotted for the metallocene hydrides \(1, 3\) and \(5\) using the computational package GaussView 5. Interaction enthalpies were corrected for basis set superposition error (BSSE) using the counterpoise method.\(^6\) In addition, the interaction energies were first calculated at the 6-31G* level with diffuse functions added to H and O and the differences between this level of theory and that with the additional polarisation function were \(\leq 0.2 \text{ kJ mol}^{-1}\).

\(^4\) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foreman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. \textit{Gaussian}, Revision B.01; Gaussian Inc: Wallingford, CT, 2009.

\(^5\) (a) Csontos, J.; Palermo, N. Y.; Murphy, R. F.; Lovas, S. \textit{J. Comput. Chem}. \textbf{2008}, \textit{29}, 1344. (b) Ruiz, E.; Salahub, D. R.; Vela, A. \textit{J. Phys. Chem}. \textbf{1996}, \textit{100}, 12265.

\(^6\) Boys, S. F.; Bernardi, F. \textit{Mol. Phys}. \textbf{1970}, \textit{19}, 553.
**Cp₂WH₂ and Cp₂TaH₃**

For the complexes Cp₂WH₂ and Cp₂TaH₃ two possible modes of binding with C₆F₅I were explored; a bifurcated interaction bridging two hydrides and side-on interaction with a single hydride (Figure 1). In order to investigate these modes, three starting geometries for Cp₂WH₂·IC₆F₅ adducts were investigated (a) an approach of C₆F₅I along the bisector of the W-H bonds and (b) W-H···I configurations with angles in the metal hydride plane of ~170° and ~190°. The initial orientation of the plane of the arene was perpendicular to the WH₂ plane. Optimisations gave minima for Cp₂WH₂·IC₆F₅ adducts both for a bifurcated (Figure S14a) and a side-on (Figure S14b) mode with the bifurcated mode found to be more stable by 1.3 kJ mol⁻¹. The counterpoise corrected binding energies for the bifurcated adduct are calculated to be -13.4 kJ mol⁻¹ and for the side on adduct -12.1 kJ mol⁻¹. The optimised geometries are shown in Figure S15 and Figure S16. For the bifurcated interaction, optimizations were also started from co-planar and perpendicular orientations of the arene relative to the WH₂ plane and converged to minima without rotation of the arene. The perpendicular geometry was calculated to be more stable by 0.3 kJ mol⁻¹.

The starting geometries for Cp₂TaH₃·IC₆F₅ adducts were from a linear Ta-Hcentral···I configuration and from Ta-Hlateral···I configurations with angles in the metal hydride plane of ~170° and ~190°. The initial orientation of the plane of the arene was perpendicular to the TaH₃ plane. Optimisations of these Cp₂TaH₃·IC₆F₅ adducts led to the location of a minimum for a bifurcated interaction (Figure S14c) with a counterpoise-corrected binding energy of -14.3 kJ mol⁻¹. Attempts to locate a minimum of a side-on interaction (Figure S14d) using tight convergence criteria were unsuccessful. The optimised geometries are shown in Figure S17.

*Figure S14: Investigated binding modes of the halogen bond donor C₆F₅I with Cp₂TaH₃ and Cp₂WH₂ where only the metal hydride plane is shown.*
Figure S15: Optimised minima for the side-on adduct of C₆F₅I with Cp₂WH₂ with cyclopentadienyl rings omitted for clarity. The colours for atoms are as follows; W blue, H light grey, C dark grey, I purple, F green. C−I⋅⋅⋅H 171.2°.

Figure S16: Optimised minima for the bifurcated adduct of C₆F₅I with Cp₂WH₂ with cyclopentadienyl rings omitted for clarity. The colours for atoms are as follows; W blue, H light grey, C dark grey, I purple, F green. C−I⋅⋅⋅H 159.5°.
Figure S17: Optimised minimum for the adduct of $\text{C}_6\text{F}_5\text{I}$ with $\text{Cp}_2\text{TaH}_3$ with cyclopentadienyl rings omitted for clarity. The colours for atoms are as follows: Ta blue, H light grey, C dark grey, I purple, F green. C−I...H$^{\text{central}}$ 173.5°. C−I...H$^{\text{lateral}}$ 152.4°.
The geometries for the calculations on Cp₂Ta(H)CO·IC₆F₅ adducts were started from linear Ta-H···I and C≡O···I configurations. The initial orientation of the plane of the arene was perpendicular to the Ta(H)CO plane. Optimisation led to the location of two minima of interaction: (a) iodine bound to hydride and (b) iodine bound to oxygen (Figure S18). The interaction energy with the hydride site was greater than that of the oxygen site by 6.0 kJ mol⁻¹. The counterpoise-corrected energy calculated for binding the hydride was -14.3 kJ mol⁻¹ compared with the energy calculated for binding the carbonyl oxygen of -8.3 kJ mol⁻¹. The optimised geometries are shown in Figure S19 and Figure S20.

Figure S18: Investigated binding modes of the halogen bond donor C₆F₅I with Cp₂Ta(H)CO where only the metal hydride plane is shown.

Figure S19: Optimised minimum for the hydride bound adduct of C₆F₅I with Cp₂Ta(H)CO with cyclopentadienyl rings omitted for clarity. The colours for atoms are as follows; Ta blue, H light grey, C dark grey, I purple, F green, O red. C–I···H 171.5°.
Figure S20: Optimised minimum for the oxygen bound adduct of $C_6F_5I$ with $Cp_2Ta(H)CO$ with cyclopentadienyl rings omitted for clarity. The colours for atoms are as follows; $Ta$ blue, $H$ light grey, $C$ dark grey, $I$ purple, $F$ green, $O$ red. $C$–$I$–$H$ 179.7°.
**Summary of calculated energies**

*Table S2: Calculated counterpoise corrected binding energies of C₆F₅I with the metallocenes studied in kJ mol⁻¹ with BSSE energies listed in brackets.*

| Mode of interaction | Bifurcated | Single site / side-on |
|---------------------|------------|-----------------------|
| Cp₂Ta(H)CO hydride bound | n/a        | -14.3(5.8)            |
| Cp₂Ta(H)CO oxygen bound | n/a        | -8.3(3.3)             |
| Cp₂TaH₃              | -13.4(5.3) | No minima located     |
| Cp₂WH₂               | -13.4(5.6) | -12.1(5.9)            |
**Comparison of calculated metal-hydride distances and angles upon binding C₆F₅I**

**Table S3: Comparison of calculated metal-hydride bond distances upon binding of C₆F₅I**

|                    | Metalloocene   | Metalloocene + C₆F₅I |
|--------------------|----------------|----------------------|
| Cp₂Ta(H)CO hydride bound | 1.758          | 1.772                |
| Cp₂TaH₃            | Ta-H<sup>central</sup>, Ta-H<sup>side</sup> | Ta-H<sup>central</sup>, Ta-H<sup>side: interacting</sup>, Ta-H<sup>side: non-interacting</sup> |
|                    | 1.758, 1.747   | 1.766, 1.747, 1.745  |
| Cp₂WH₂ (bifurcated) | 1.694          | 1.695                |
| Cp₂WH₂ (side)      | 1.694          | 1.692, 1.700         |

**Table S4: Comparison of calculated metal-hydride angles upon binding of C₆F₅I**

|                    | H-M-X (X = H, CO) Angles (°) |
|--------------------|-------------------------------|
|                    | Metalloocene     | Metalloocene + C₆F₅I                       |
| Cp₂Ta(H)CO hydride bound | 91.06          | 92.64                                      |
| Cp₂TaH₃            | 63.08            | Ta-H<sup>central-side: interacting</sup>, Ta-H<sup>central-side: non-interacting</sup> |
|                    | 64.59, 62.48     |                                            |
| Cp₂WH₂ (bifurcated) | 77.22            | 80.70                                      |
| Cp₂WH₂ (side)      | 77.22            | 76.30                                      |
Electrostatic potential plots for Cp₂TaH₃, Cp₂WH₂ and Cp₂Ta(H)CO

Figure S21: Electrostatic potential plot of Cp₂TaH₃ in the TaH₃ plane. Contours are labelled in kJ mol⁻¹. Negative contours in red; positive contours in yellow.

Figure S22: Electrostatic potential plot of Cp₂WH₂ in the WH₂ plane. Contours are labelled in kJ mol⁻¹. Negative contours in red; positive contours in yellow.
Figure S23: Electrostatic potential plot of $\text{Cp}_2\text{Ta(H)CO}$ in the Ta(H)CO plane. Contours are labelled in kJ mol$^{-1}$. Negative contours in red; positive contours in yellow.

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Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Revision B.01; Gaussian Inc: Wallingford, CT, 2009.

Cartesian coordinates and total energies for computed stationary points

$\text{Cp}_2\text{Ta(H)CO} \ E = -557.638646434 \text{ au}$

|   | C     | C    | H     | H     | C    |
|---|-------|------|-------|-------|------|
|   | 1.895176531300 | 0.650047980646 | 0.614788008979 |
|   | 1.6752907088816 | -0.662016885816 | 1.094188011368 |
|   | 2.233548464393  | 0.538248441018  | -0.768774247817 |
|   | 1.903076777224  | -1.572739926853 | 0.024626124968 |
|   | 2.255709139066  | -0.830163356556 | -1.112183154166 |
|   | 1.880929689170  | 1.552690447482  | 1.193175826691 |
|   | 1.431142964020  | -0.929432345351 | 2.104531999147 |
|   | 2.479862968119  | 1.350218629396  | -1.425379801764 |
|   | 1.82244628403   | -2.64226839310  | 0.076874661577 |
|   | 2.467143377749  | -1.22866263548  | -2.084509401473 |
|   | -2.093249303822 | 0.188012953779  | 0.698029696398 |
C  -1.559800015843  -1.036784144730  1.161703112122  1.161703112122
C  -2.453786185833  -0.004746904593  -0.670945196860
C  -1.617296434488  -1.980550921472  -1.019679686891
H  -2.261854960985  1.072770964897  1.279643328052
H  -1.21963475284  -1.236513014349  2.159852610640
H  -2.90595678459  0.726309763904  -1.312971006909
H  -1.292293090566  0.030392020266  0.141872793349
H  -2.33139710886  -1.784533038438  -1.984361493388
Cp   Ta(CO)H\textsuperscript{\textsuperscript{2}}\textsuperscript{\textsuperscript{Ta}}\textsuperscript{\textsuperscript{IC}}\textsuperscript{\textsuperscript{6}}\textsuperscript{F}\textsuperscript{\textsuperscript{5}} – Hydride bound. Counterpoise corrected binding energy = -1296.4592483266 au, BSSE = 0.002208677 au
C  -0.329317951183  1.791466670854  -0.986562155901
O  -0.426911348163  2.915075647306  -1.198708671110

Cp\textsuperscript{2}Ta(CO)H\textsuperscript{\textsuperscript{2}}\textsuperscript{Ta}IC\textsuperscript{6}F\textsuperscript{5} – Hydride bound. Counterpoise corrected binding energy = -1296.4592483266 au, BSSE = 0.002208677 au
C  -1.888544947545  0.656599281048  0.596032350800
C  -1.667518258783  -0.649005298838  1.091873796886
C  -2.33098455267  0.527279150284  -0.784695118191
C  -1.901600568917  -1.573808507650  0.035879620546
C  -2.259129111202  -0.84614195266  -1.108727563699
H  -1.871297253874  1.566778783797  1.162581548449
H  -1.419713906983  -0.903168864440  2.104708740042
H  -2.485138936555  1.330206500042  -1.450302829350
H  -1.82285680032  -2.64268711379  0.102253673933
H  -2.47695594726  -1.257546300078  -2.07450328153
C  -2.08907502794  0.195821510409  0.679104073660
C  -1.555316561559  -1.02234278523  1.159149019098
C  -2.451509367910  -0.015407631963  -0.686916359524
C  -1.615141268401  -1.981199532552  0.109295528151
C  -2.17631406114  -1.359966453162  -1.016140329080
C  -2.256970159418  1.088551954558  1.248741518639
C  -1.214502684092  -1.208311497588  2.156999347080
C  -2.097550703656  0.705488724893  -1.337750311310
H  -1.291553791876  -3.003469483631  0.167278891920
C  -2.333960130546  -1.814871169235  -1.974073642645
Ta  -0.050490223239  -0.207468589209  -0.494687937066
H  -0.272465363080  -0.711138298406  -2.18764130115
C  -0.292066013896  1.786985413319  -0.999189513559
O  -0.426504504876  2.910744585500  -1.203164011041
I  -0.191759084423  0.238478534659  -4.787474151187
C  -0.287377238153  0.692335047599  -6.849420827185
C  -1.496938526575  0.710098196154  -7.51911840240
C  -0.857487715540  0.98245047056  -7.568268481011
C  -0.803492630894  1.282963276038  -8.915611430497
C  -0.413941127066  1.295477732926  -9.565372669495
C  -1.568483745513  0.008183405757  -8.866098371640
F  2.045244775253  0.981431514206  -6.984964057538
F  1.911832959371  1.557518137550  -9.584594811981
F  -0.473916827156  1.581112042136  -10.853404315921
F  -2.736819473590  1.01899379639  -9.487558010807
F  -2.627889097025  0.440075736964  -6.887416218214
Cp$_2$Ta(H)CO-IC$_6$F$_5$ – Oxygen bound. Counterpoise corrected binding energy = -1296.456983428 au, BSSE = 0.0012722825 au

C  3.983536222384  -2.015078589030  -1.058673358235
C  5.282682222369  -1.633706233321  -0.653267065244
C  3.259521087917  -2.359415780484  0.123587049793
C  5.367053495558  -1.769666334864  0.760682386505
C  4.125969235403  -2.225435893800  1.2298721211340
H  3.626773234118  -2.095636136433  -2.066567039982
H  6.084397944946  -1.342199186198  -1.304610267357
H  2.427384047265  -2.713126086196  0.163146847681
H  6.23036387169  -1.562832468402  1.364968731950
H  3.866871560670  -2.406354863364  2.254082632175
C  3.9836838311228  2.015089120881  -1.058722849105
C  5.28549834255  1.633843147017  -0.65302236051
C  3.259317613133  2.359393811648  0.123526202807
C  5.366899426823  1.769843159935  0.760643534984
C  4.125771742165  2.225513612572  1.229817625062
H  3.626598106497  2.095580500481  -2.06619271663
H  6.084287400792  1.342381650961  -1.304634398267
H  2.427151758861  2.713023474448  0.163071183704
H  6.23019930297  1.563104878066  1.36493225732
H  3.866649904466  2.406421234879  2.254024680705
Ta  3.779324240178  0.000008846040  0.212594608975
H  3.10267371794  -0.000009058242  1.83367131821
C  1.89652715908  -0.000072773824  -0.627721656848
O  0.874249525440  -0.000116024568  -1.16275023848
C  -4.323208893142  -0.00019492514  -0.114078654086
C  -5.019417834413  -1.186922835348  0.026814939460
C  -6.373366973172  -1.194353730434  0.300738481526
C  -7.051024025421  0.000057842127  0.43786711341
C  -6.373304563070  1.194430992895  0.300712345218
C  -5.019358376665  1.186922830176  0.026789003027
F  -7.021407118711  -2.340120285049  0.431822402403
F  -8.344965082683  0.00094543196  0.69967988241
F  -7.021284775776  2.340234346980  0.431771131204
F  -4.408161825183  2.352336981637  -0.096847976515
F  -4.408284750666  -2.352571097846  -0.096796579040
I  -2.622972703995  -0.000077327398  -0.530249100254

Cp$_3$TaH$_3$ E = -445.535453128 au

C  -2.139164  0.030226  1.145221
C  -1.694326  1.292387  0.709812
C  -2.387942  -0.763048  0.000001
C  -1.694325  1.292389  -0.709801
C  -2.139164  0.030231  -1.145214
H  -2.260872  -0.281367  2.163305
H  -1.424769  2.117723  1.341408
H  -2.726459  -1.780109  -0.000001
H  -1.424768  2.117728  -1.341393
H  -2.260870  -0.281358  -2.163300
Cp₃TaH₂IC₂F₅ – bifurcated interaction. Counterpoise corrected binding energy = -1184.3557096063 au, BSSE = 0.0020143235 au
\[
\text{Cp}_2\text{WH}_2 \text{E} = -454.98949983 \text{ au}
\]

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| F    | -2.241707  | -9.267575  | -0.456691  |
| C    | -3.862637531727 | 1.807797784572 | -1.159543375908 |
| C    | -4.655860481128  | 1.554448001796  | 0.000000073471 |
| C    | -2.89450167588  | 2.228708930071  | 0.703727218249 |
| C    | -3.862638208288  | 1.807796600101  | 1.159545731171 |
| C    | -2.58945060606  | 2.228708728574  | 0.703721070105 |
| H    | -4.18152848484  | 1.757776909284  | -2.181679308102 |
| H    | -5.691413180196  | 1.748022681313  | 0.000000028452 |
| H    | -1.752645790215  | 2.47357750609  | -1.326592821930 |
| H    | -4.181529686466  | 1.75773591808  | 2.181681418467 |
| H    | -1.75264650923  | 2.47355590519  | 1.326597541464 |
| C    | -3.862637098138  | -1.807796995242 | -1.159544754855 |
| C    | -4.655860558999  | -1.554447963737 | -0.000000800760 |
| C    | -2.894499595558  | -2.22870849763  | -0.70372863808 |
| C    | -3.862638007016  | -1.80779699637  | 1.159544353516 |
| C    | -2.589450983746  | -2.22870893935  | 0.703730025697 |
| H    | -4.181527599012  | -1.75775530930  | -2.181680797515 |
| H    | -5.691413245915  | -1.74802185111  | 0.000001572832 |
| H    | -1.752645313930  | -2.47357052212  | -1.32659625952 |
| H    | -4.181530727303  | -1.75774879100  | 2.181679930696 |
| W    | -3.09788775593  | -0.000000111116 | -0.000000139309 |
| H    | -1.686256696298  | -0.000000376557 | 1.056967248890 |
| H    | -1.686257430289  | 0.000000386456  | -1.056968427520 |

\[
\text{Cp}_2\text{WH}_2-I\text{C}_6\text{F}_6 - \text{side on interaction, Counterpoise corrected binding energy} = -1193.809268202477 \text{ au, BSSE} = 0.002229908943 \text{ au}
\]

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| C    | -2.471603809541  | -1.733075212270  | 0.912165097489 |
| C    | -3.824830791458  | -1.423649423697  | 1.241521692458 |
| C    | -2.469330856168  | -2.181378024550  | -0.431929103536 |
| C    | -4.641541988890  | -1.672064243689  | 0.097439954229 |
| C    | -3.787124864570  | -2.149301339310  | -0.924925331040 |
| H    | -1.625230544037  | -1.70501785373  | 1.569232838492 |
| H    | -4.177226645893  | -1.109578413179  | 2.204659789085 |
| H    | -1.602818429026  | -2.476576755864  | -0.99101461367 |
| H    | -5.707808389358  | -1.579976607098  | 0.035554159912 |
| H    | -4.087012480628  | -2.408958632244  | -1.92077943532 |
| C    | -2.397926574243  | 1.911884579601  | 0.824657748030 |
| C    | -3.762226137591  | 1.673519012450  | 1.167166059746 |
| C    | -2.378780995814  | 2.296536216051  | -0.539476981240 |
| C    | -4.569347625145  | 1.899550096371  | 0.011694281450 |
| C    | -3.697345581076  | 2.292299804080  | -1.031557678583 |
| H    | -1.552739996777  | 1.881218273178  | 1.483134903737 |
| H    | -4.126084514911  | 1.420498108865  | 2.143918808749 |
| H    | -1.501668752859  | 2.527543445126  | -1.11152212106 |
| H    | -5.638521243162  | 1.847738328559  | -0.046736422516 |
| H    | -3.987467599973  | 2.51578376310  | -2.03901187994 |
| W    | -3.189913416409  | 0.07578809751  | -0.334566921176 |
| H    | -3.699093656705  | 0.047353550102  | -1.947669664077 |
Cp₂WH₂·IC₆F₅ – bifurcated interaction, Counterpoise corrected binding energy = -1193.8097703908 au, BSSE = 0.0021497169 au