Supporting Information

Dihydrogen bonding vs. metal-sigma interaction in complexes between H_2 and metal hydride

by

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Table S1. Geometrical parameters (in Å) for complexes with two hydrogen molecules, H_2(···M) designates the H-H bond length for H_2 molecule that are in contact with the metal centre, H···M is the hydrogen-metal distance, H_2(···H) concerns the H-H bond distance involved in DHB while H···H is the intermolecular distance for DHB. Bolded values correspond to trimers while non-bolded (in the second line) concern dimers.

The level	H_2(···M)	Me-H^*	H···M*	H_2(···H)	Me-H^^*	H···H
H_2···LiH···H_2						
MP2/aug-cc-pVTZ	**0.7412** 0.7412	**1.6069** 1.6071	**2.1818** 2.1809	**0.7404** 0.7403	**1.6069** 1.6039	**2.6036** 2.6000
MP2/aug-cc-pQTZ	**0.7401** 0.7401	**1.6057** 1.6060	**2.1789** 2.1812	**0.7393** 0.7392	**1.6057** 1.6025	**2.6061** 2.6004
CCSD/aug-cc-pVTZ	**0.7467** 0.7467	**1.6116** 1.6123	**2.1859** 2.1858	**0.7456** 0.7455	**1.6116** 1.6097	**2.6246** 2.6366
H_2···NaH···H_2						
MP2/aug-cc-pVTZ	**0.7395** 0.7394	**1.9217** 1.9219	**2.7580** 2.7626	**0.7409** 0.7407	**1.9217** 1.9187	**2.5978** 2.6030
MP2/aug-cc-pQTZ	**0.7383** 0.7383	**1.9210** 1.9214	**2.7555** 2.7626	**0.7398** 0.7397	**1.9210** 1.9178	**2.6001** 2.6037
CCSD/aug-cc-pVTZ	**0.7449** 0.7450	**1.9291** 1.9294	**2.7767** 2.7614	**0.7458** 0.7457	**1.9291** 1.9262	**2.6556** 2.6609
H_2··· HBeH···H_2						
MP2/aug-cc-pVTZ	**0.7391** 0.7391	**1.3299** 1.3301	**2.8918** 2.8975	**0.7381** 0.7381	**1.3299** 1.3292	**2.6596** 2.6718
MP2/aug-cc-pQTZ	**0.7383** 0.7380	**1.3281** 1.3280	**2.8619** 2.8975	**0.7372** 0.7370	**1.3281** 1.3274	**2.7674** 2.6736
CCSD/aug-cc-pVTZ	**0.7444** 0.7445	**1.3336** 1.3337	**2.9276** 2.8981	**0.7435** 0.7435	**1.3336** 1.3328	**2.6776** 2.6863

* mean values are included for H_2··· HBeH···H_2 complex where two H···M contacts and Be-H bonds are not always equivalent

^ non-bolded value for a complex with H_2···M interaction

^^ non-bolded value for a complex with H-H···H-M interaction

Table S2. The NBO charges (in au), A and C designate H_2 molecules, A that one being in contact with Me while C that one participating in DHB, B is the metal hydride, NBO energies (in kcal/mol) are also included, bolded values concern trimers while those in the second line (non-bolded) concern dimers.

Complex	Charge - A	Charge - B	Charge - C	NBO energy AB	NBO energy BC
$H_2\cdots LiH\cdots H_2$	**0.0216** 0.0216	**-0.0165**	**-0.0051** -0.0050	**6.65** 6.61	**1.76** 1.65
$H_2\cdots NaH\cdots H_2$	**0.0080** 0.0080	**-0.0001**	**-0.0079** -0.0077	**2.75** 2.74	**2.19** 2.10
$H_2\cdots HBeH\cdots H_2$	**0.0047** 0.0046	**-0.0043**	**-0.0005** -0.0007	**1.80** 1.77	**0.77** 0.23