

# The tri- $\mu$ -hydrido-bis[( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)aluminum(III)] theoretical study, the assets of sandwiched M<sub>2</sub>H<sub>3</sub> (M of 13th group elements) stability

Abdeladim Guermoune · Al Mokhtar Lamsabhi ·  
Driss Cherqaoui · Abdellah Jarid · Hafid Anane ·  
Gabriel Merino

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**Abstract** The stability of the tri- $\mu$ -hydrido-bis[( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)aluminum], Cp\*<sub>2</sub>Al<sub>2</sub>H<sub>3</sub>, **1** is studied at B3LYP/6-311+G(d,p), CCSD(T)/B3LYP/6-311+G(d,p) and MP4//B3LYP/6-311+G(d,p) levels. The coordination between Al<sub>2</sub>H<sub>3</sub> entity and both C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub> groups is ensured by strong electrostatic and orbital interactions. The orbital analysis of the interacting fragments shows that Al<sub>2</sub>H<sub>3</sub> acceptor, which keeps its tribridged structure, implies the vacant (*a*'<sub>1</sub>) and five antibonding (*a*'<sub>2</sub>, *e*' and *e*'') molecular orbitals to interact with two orbitals mixtures, *b*<sub>1</sub> and *e*' of the donors (C<sub>5</sub>Me<sub>5</sub>). When we take into account the solvent effect, the computation shows that **1** seems to be stable in condensed phase with a tribridged bond between the Al atoms [Cp\*Al( $\mu$ -H)<sub>3</sub>AlCp\*], whereas in the gas phase, the monobridged Cp\*AlH( $\mu$ -H)AlHCp\* **4** is slightly favored (4 kcal mol<sup>-1</sup>). We propose that **1** could be prepared thanks to Cp\*Al (**2**) and Cp\*AlH<sub>2</sub> (**3**) reaction in acidic medium.

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A. Guermoune · A. M. Lamsabhi · D. Cherqaoui · A. Jarid (✉) ·  
H. Anane  
Département de Chimie, Faculté des Sciences Semlalia,  
Université Cadi Ayyad,  
B.P. 2390 Marrakech, Morocco  
e-mail: jarid@ucam.ac.ma

G. Merino  
Facultad de Química, Universidad de Guanajuato,  
Noria Alta s/n CO 36050,  
Guanajuato Gto, México

A. M. Lamsabhi  
Universidad Autónoma de Madrid,  
Ciencias, C-9 Dpto. Química, Cantoblanco,  
Ctra. Comlenar km-15,  
E-28049 Madrid, Spain

The experimental treatment of this type of metallocenes would contribute to the development of the organometallic chemistry of 13th group elements.

**Keywords** (C<sub>5</sub>(Me)<sub>5</sub>)<sub>2</sub>Al<sub>2</sub>H<sub>3</sub> · Coordination · Decamethylcyclopentadienyl · DFT calculation · Dimetalloenes

## Abbreviation

Cp Cyclopentadienyl(C<sub>5</sub>H<sub>5</sub>)  
Cp\* Pentamethylcyclopentadienyl(C<sub>5</sub>Me<sub>5</sub>)  
PES Potential energy surface  
DFT Density functional theory  
3c-2e Three centres-two electrons

## Introduction

Since their discovery in 1951 [1], the “metallocenes”, compounds where a metallic atom gets “sandwiched” between two cyclopentadienyl groups, have not ceased drawing the chemists’ attention. Currently, this attention is focused on dimetalloenes which are characterized by two sandwiched metallic atoms between the pentadienic rings, especially since the convinced characterization of the decametyldizincocene, Cp\*Zn–ZnCp\* (Cp\* = C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>) by Carmona *et al.* [2]. The most relevant point discussed in recent works is the M–M bond properties. Schaefer *et al.* [3–5] have studied theoretically other complexes CpM–M’Cp (M and M’ of main group elements) and recommended their synthesis. Kan [6] has studied the nature of the M–M (M=Zn, Cd, Hg) bond using an energy decomposition analysis whereas Philpott and Kawazoe [7] have rationalized, on the same series, the effect of the rings hapticity on

the metal-metal bond. A slight disagreement concerning the M–M bond nature has been noticed when one performs the electronic localization analysis and is (M–M bond) still a subject of controversy [8, 9]. In another work, heteronuclear dimetallocenes Cp\*E–E'Cp\* (E from group13, and E' from alkaline group) were investigated in the donor–acceptor context [10].

In this paper, we discuss the ability of sandwiched alane Al<sub>2</sub>H<sub>3</sub> to be stable in the context of high coordination of the 13th group elements. The hydride compounds based on these elements have many varied chemical properties by their Lewis acid or base behaviors. However, depending on the electronic configuration, it can form all bond types:  $\sigma$ ,  $\pi$ , three-centers-two-electrons (3c-2e), and coordination. In previous works on Al<sub>2</sub>H<sub>3</sub><sup>−</sup> anion [11, 12], it has been shown that the Al( $\mu$ -H)<sub>3</sub>Al was, energetically, the most stable compared to mono and double-bridged structures on the total potential energy surface (PES).

On the other hand, the preparation of the decamethylaluminocenium [Cp\*<sub>2</sub>Al]<sup>+</sup> and the aluminocenium Cp<sub>2</sub>Al<sup>+</sup> cations have been prepared by Schnöckel *et al.* [13] and Bochmann *et al.* [14] respectively. In these compounds the Al(III) atom can be considered as hexacoordinated (6 *l*-type ligands, C=C) or as decacoordinated (10 *X*-types ligands) [15]. The valence isomerization of the multi-coordinated 13th group elements bond has been the subject of studies of Cowley *et al.* [16–18]. These results open the way to consider other complexes of 13th group elements in high coordinated states.

Himmel and Vollet [19] reported that the Cp\*Al (**2**) and Cp\*AlH<sub>2</sub> (**3**) compounds have been observed by IR spectroscopy. They also unsuccessfully tried to isolate the [Cp\*Al]<sub>2</sub> and [Cp\*AlH<sub>2</sub>]<sub>2</sub> dimers. In the same work, computational treatment of these compounds, at DFT-BP/TZVPP level, has been performed where the energetic and structural data did not support the stability of these dimers. The Al–Al bond has been computationally shown longer than that of the crystal. However, the ionic or neutral Al<sub>2</sub> entity, could not be sandwiched between two Cp\* groups. Let's remember that the Cp...M (M of main group) interaction is well known to include discrete [MCp<sub>n</sub>](n=1–3) molecules, polymeric structures with [...M-Cp-M...] unit, and [MCp]<sub>n</sub> (n=4–6) clusters [20–24]. One should wonder about a supported Al–Al sandwiched bond. As it's so for transition metals [25–28], can Al( $\mu$ -H)<sub>3</sub>Al be

sandwiched between two Cp\* ligands? If the dimetallocenes complexes became obvious in the organometallic chemistry for transition metals, no equivalent of main group elements have been known until today. Moreover, to our knowledge there is no theoretical study concerning this type of systems implying elements of 13th group with bridged bond according to 3c-2e model.

Considering the aforementioned discussion, the objective of this work is to study the tri- $\mu$ -hydrido-bis[( $\eta$ <sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)aluminum(III)] complex, where the Al<sub>2</sub>H<sub>3</sub> entity is sandwiched between two Cp\*. The proposed species are of importance, not only because of their ability to act as precursor to metal or semiconductor compounds, but also because of their structural diversity [29]. We present a theoretical prediction of the structural features and energetic stability of this complex.

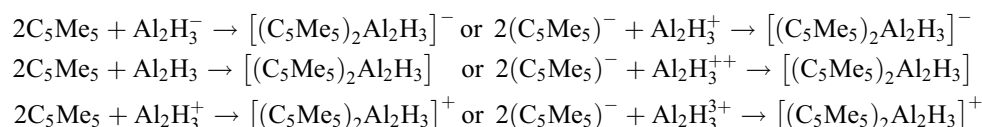
### Computational details

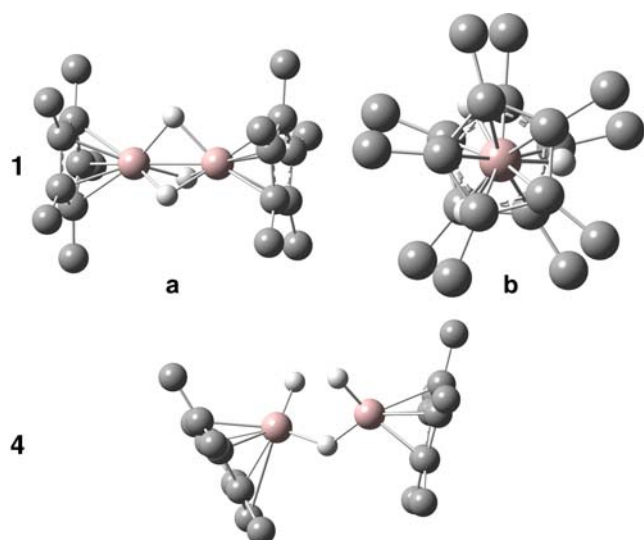
Calculations were performed using the density functional theory (DFT) by means of the B3LYP [30–32] functional and the 6–311+G(d,p) basis set for all atoms. Geometries optimizations were done without restrictions (C<sub>1</sub> symmetry). Each structure is characterized by a vibrational calculation by diagonalizing the second derivative matrix of the energy. In order to test the accuracy of the DFT calculations, we have evaluated absolute and complexation energies, taking the Cp<sub>2</sub>Al<sub>2</sub>H<sub>3</sub> (Cp = C<sub>5</sub>H<sub>5</sub>) as model, at CCSD(T) [33] and MP4 [34] levels using the B3LYP//6–311+G(d,p) geometries. The NBO partitioning scheme [35] has been adopted to evaluate the charge transfer. Concerning the solvent effect and in order to decide between two close structures, we carried out the Tomasi model [36–38]. To perform these calculations, we used the Gaussian03 series [39].

### Results and discussion

#### Stability of the Cp\*Al( $\mu$ -H)<sub>3</sub>AlCp\* complex

Although Cp\*<sub>2</sub>Al<sub>2</sub>H<sub>3</sub> would be cationic (in accordance with the Al(III) electronic counting) we have examined the neutral and anionic complexes which are considered results of following hypothetical reactions.





**Fig. 1**  $[(\eta^5\text{-C}_5\text{H}_5)\text{Al}(\mu\text{-H})_3\text{Al}(\eta^5\text{-C}_5\text{H}_5)]^+$  equilibrium structures **1** (favored in condensed phase), **a**) lateral view **b**) axial view and  $[(\eta^5\text{-C}_5\text{H}_5)\text{AlH}(\mu\text{-H})\text{AlH}(\eta^5\text{-C}_5\text{H}_5)]^+$  **4** (favored in gas phase)

The optimizations have been carried out without geometrical restrictions ( $C_1$  symmetry). No ideal conformation (staggered or eclipsed) was energetically favored for the cationic (Fig. 1) and the neutral compounds but in the anionic case, the two  $\text{Cp}^*$  are in an eclipsed arrangement. This is probably due to a competitiveness between steric hindrance and electrostatic effects between  $\text{Al}_2\text{H}_3(D_{3h})$  and  $[\text{Cp}^*\dots\text{Cp}^*](D_{5h})$  entities. Moreover, in all cases the  $\text{Al}_2\text{H}_3$  fragment does not lose its identity (tribridged) as in isolated state.

The second derivative energy matrix analysis shows that the neutral and cationic forms of **1** are minima on the total PES, whereas the anionic one is a transition state ( $\nu_{\text{imaginary}} = -334.4 \text{ cm}^{-1}$ ). The corresponding normal mode involves the deviation of the  $\text{H}_3$  entity from the middle position along the centroid–Al–Al–centroid axis (centroid = pentagon center). This movement is accompanied with the

hapticity reduction of one  $\text{Cp}^*$  group leading to the  $[\text{H}_3\text{Al}(\eta^1\text{-Cp}^*)]^-$  fragment where the aluminum atom is covalently bound to one C atom of the ring, and to  $\text{AlCp}^*$  moiety where the aluminum remains on the  $\text{C}_5$  axis of the  $(\eta^5\text{-Cp}^*)$  ligand.

The stability of the  $\text{Al}_2\text{H}_3$  fragment within the complex could be qualitatively rationalized, in accordance with the above hypothetical reactions, by the complexation energy. This approach should be cautiously considered because the complexes formation does not occur *via* such reactions. Hence, this energy, which is calculated as the difference between the complex and the sum of isolated fragments ( $\text{Al}_2\text{H}_3$  and two decamethylcyclopentadienyls) energies, should not be taken as the necessary energy to form the complex. This energy increases ongoing from the anionic to the cationic compound (Table 1). This evolution is due to both electrostatic and orbital interactions, which increase in the same direction. It exhibits rather high values when we consider the anionic  $\text{C}_5\text{H}_5^-$  and cationic  $\text{Al}_2\text{H}_3^q$  ( $q=1-3$ ) reactants in the case of the  $(\eta^5\text{-C}_5\text{H}_5)\text{Al}(\mu\text{-H})_3\text{Al}(\eta^5\text{-C}_5\text{H}_5)$  model (Table 2). The same trend is observed at the three levels, B3LYP/6–311+G(d,p), MP4//B3LYP/6–311+G(d,p), and CCSD(T)//B3LYP/6–311+G(d,p) of theory.

The molecular orbital analysis of the  $\text{Cp}_2\text{Al}_2\text{H}_3$  model shows that the Cp–Cp entity implies the in-phase  $e'$  (or  $a_1$  and  $b_1$  in  $C_{2v}$  symmetry) and  $a'_1(a_1)$ , and the out-of-phase  $e''(a_2, b_2)$  and  $a'_2(b_2)$  combinations [40] to interact with the corresponding orbitals of the  $\text{Al}_2\text{H}_3$  fragment having the appropriate symmetry. Let's take for example, the cationic complex, which is considered as a result of the coordination of  $\text{Al}_2\text{H}_3^{3+}$  with  $[\text{Cp}\dots\text{Cp}]^{2-}$  entity (or  $\text{Al}_2\text{H}_3^+$  with  $\text{Cp}\dots\text{Cp}$ ). We depict the main orbital interactions diagram in Fig. 2 (a) and the electronic density (b). The well expected  $a'_1$  orbital of  $\text{Al}_2\text{H}_3^{3+}$  which has the equivalent vacant orbital properties of the alane ( $\text{AlH}_3$ ) [41], interacts with the  $a'_1$  one of cyclopentadienyls. The two  $\pi^*$  ( $p_x\text{-}p_x$  and  $p_y\text{-}p_y$  of Al atoms) with  $e''$  symmetry ( $D_{3h}$ ) interact

**Table 1** Energy E (au) of fragments and complexes, complexation energy  $E_c$  ( $\text{kcal mol}^{-1}$ ) of complexes and selective geometrical parameters of isolated and sandwiched  $\text{Al}_2\text{H}_3$  fragment

Compound	Energy	$E_c$	Al–Al	Al–H	$^a\angle\text{H}_b\text{-Al-Al}$	$^b d_{\text{X-Al}} (\text{\AA})$
$\text{Al}_2\text{H}_3^-$	–486.72483		2.589	1.801	44.05	—
$\text{Al}_2\text{H}_3$	–486.664348		2.461	1.784	46.39	—
$\text{Al}_2\text{H}_3^+$	–486.394270		2.356	1.774	48.4	—
$\text{C}_5(\text{CH}_3)_5$	–390.16217		—	—	—	—
$\text{Cp}^*\text{AlH}_2$	–633.85416		—	1.593	—	—
$\text{Cp}^*\text{AlH}^+$	–633.04291		—	1.546	—	—
$[\text{Cp}^*_2\text{Al}_2\text{H}_3]^-$	–1267.12874	$^c 49.93$	2.579	1.835	45.33	2.276
$\text{Cp}^*_2\text{Al}_2\text{H}_3$	–1267.08510	$^c 60.50$	2.501	1.802	46.10	1.978
$[\text{Cp}^*_2\text{Al}_2\text{H}_3]^+$	–1266.93172	$^c 133.73$ $^d 21.74$	2.365	1.753	47.74	1.804

$^a$   $\text{H}_b$ : bridged hydrogen of  $\text{Al}_2\text{H}_3$  fragment.  $^b$  X: Center of  $\text{Cp}^*$ .

$^c$  difference:  $E([\text{Cp}^*_2\text{Al}_2\text{H}_3]^q) - 2E(\text{Cp}^*) - \text{Al}_2\text{H}_3^q$ , ( $q=-1, 0, 1$ ).

$^d$  difference:  $E([\text{Cp}^*_2\text{Al}_2\text{H}_3]^+) - E([\text{Cp}^*\text{AlH}]^+) - E(\text{Cp}^*\text{AlH}_2)$

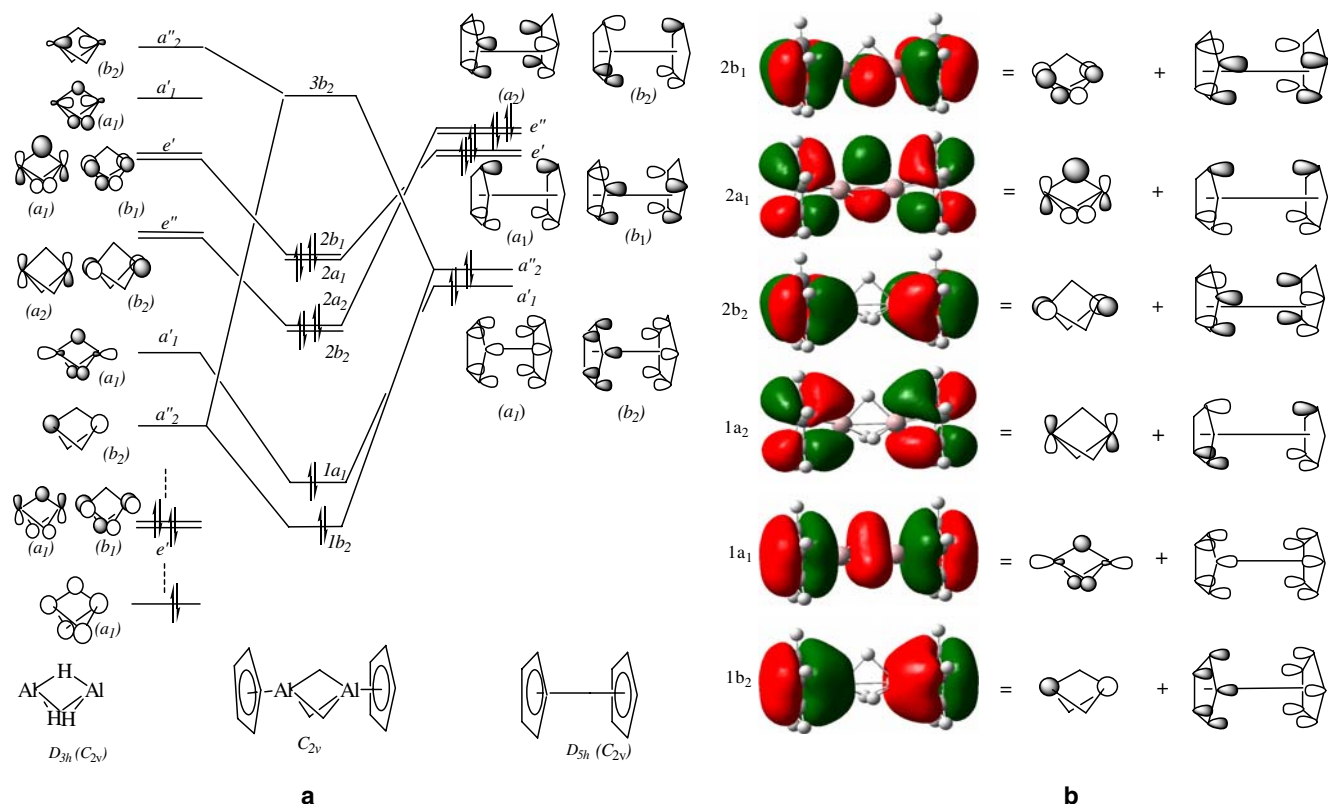
**Table 2** Energy E(au) of fragments and complexes models  $\text{Cp}_2\text{Al}_2\text{H}_3$ , and complexation energy  $E_c(\text{kcal mol}^{-1})$  at B3LYP//6–311+G(d,p) (DFT), CCSD(T)/DFT and MP4//DFT levels

Compound	E			Ec		
	B3LYP	MP4*	CCSD(T)*	B3LYP	MP4*	CCSD(T)*
$\text{Al}_2\text{H}_3^{+++}$	–485.03572	–484.07121	–484.07300			
$\text{Al}_2\text{H}_3^{++}$	–485.84419	–484.85353	–484.85576			
$\text{Al}_2\text{H}_3^+$	–486.39427	–485.40066	–485.40307			
$\text{Al}_2\text{H}_3$	–486.66435	–485.65522	–485.65885			
$\text{Al}_2\text{H}_3^-$	–486.72483	–485.70636	–485.70952			
$\text{C}_5\text{H}_5^-$	–193.58078	–192.93550	–192.93349			
$\text{C}_5\text{H}_5$	–193.51575	–192.89490	–192.90523			
$[\text{Cp}_2\text{Al}_2\text{H}_3]^-$	–873.86853	–871.55822	–871.63500	–196.22 <sup>a</sup>	–179.82 <sup>a</sup>	–229.00 <sup>a</sup>
				–70.41 <sup>b</sup>	–38.94 <sup>b</sup>	–72.17 <sup>b</sup>
$\text{Cp}_2\text{Al}_2\text{H}_3$	–873.81345	–871.53724	–871.60982	–506.84 <sup>a</sup>	–509.99 <sup>a</sup>	–556.65 <sup>a</sup>
				–73.80 <sup>b</sup>	–57.87 <sup>b</sup>	–88.16 <sup>b</sup>
$[\text{Cp}_2\text{Al}_2\text{H}_3]^+$	–873.63719	–871.39180	–871.46110	–903.55 <sup>a</sup>	–909.63 <sup>a</sup>	–954.51 <sup>a</sup>
				–132.67 <sup>b</sup>	–126.34 <sup>b</sup>	–155.35 <sup>b</sup>
				(–18.7) <sup>c</sup>	(–28.5) <sup>c</sup>	(–28.9) <sup>c</sup>

\* using 6–31G(d,p) basis set.  
<sup>a</sup> from  $2\text{C}_5\text{H}_5^-$ , <sup>b</sup> from  $2\text{C}_5\text{H}_5$  and  $\text{Al}_2\text{H}_3^{+++}$ . <sup>c</sup> Values calculated as  $E([\text{Cp}_2\text{Al}_2\text{H}_3]^+) - [E(\text{CpAlH}_2) + E(\text{CpAlH}^+)]$  difference. To compare these values we discuss them without negative sign

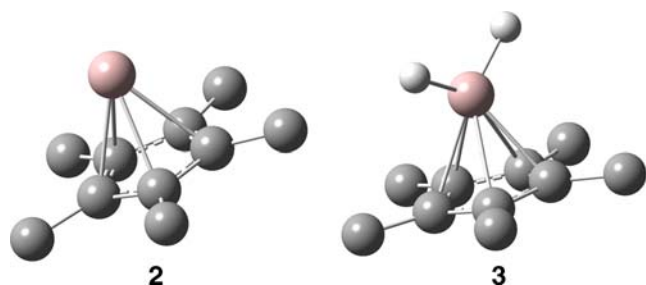
with the out-of-phase combination of the degenerated HOMO of the rings. As the cationic central fragment lacks more electrons, the  $\sigma_s^*(\text{Al} - \text{Al})$  which is the LUMO ( $a_2''$ ) intervenes in the coordination by interacting with the out-of-phase combination of  $\text{HOMO}_{-2}$  of both cyclopenta-

dienyls. The same interaction has a repulsive character in the neutral and anionic complexes because the  $\sigma_s^*(\text{Al} - \text{Al})$  becomes occupied by one and two electron (s) respectively leading to the filling of the corresponding antibonding orbital  $3b_2$  ( $C_{2v}$  symmetry). This is justified



**Fig. 2** (a) Main interactions diagram of  $[\text{Cp}_2\text{Al}_2\text{H}_3]^+$ . Both Cp constitute one fragment which interacts with  $\text{Al}_2\text{H}_3^{3+}$ . The parenthetic symmetry labels correspond to the  $C_{2v}$  group. For clarity's sake the pz orbitals of C atoms are represented only by one lobe. (b) Electronic density contour plot





**Fig. 3** Optimized structures of  $\text{Cp}^*\text{Al}$  and  $\text{Cp}^*\text{AlH}_2$ . The hydrogen atoms of methyl groups are omitted for clarity

by the lengthening of Al–Al bond as well in the isolated  $\text{Al}_2\text{H}_3$  state (2.356, 2.461, 2.589 Å) as in the complexed state (2.365, 2.501, 2.579 Å) for anion, neutral, and cation respectively (Table 1). On the other hand, the electrostatic contribution decreases because of the decreasing of  $\Delta q$  (donor and acceptor charges difference). This clearly supports the decreasing of their above complexation energy in the direction cation, neutral, anion.

These interactions are not accompanied by any significant change of the  $\text{Al}_2\text{H}_3$  structural identity upon complexation. In fact, we note for cationic and neutral complexes that the Al–Al bond length ( $d_{\text{Al–Al}}$ ), increases weakly by 0.009 and 0.04 Å respectively whereas,  $d_{\text{Al–H}}$  decreases for cationic complex (0.021 Å) and increases for neutral (0.018 Å) (Table 1). These two bond-lengths variation occur without significant change of  $\angle\text{H–Al–Al}$  angle. In anionic complex case,  $d_{\text{Al–Al}}$  decreases slightly by 0.01 Å while  $d_{\text{Al–H}}$  and  $\angle\text{H–Al–Al}$  increase from isolated  $\text{Al}_2\text{H}_3^-$  to complexed state. Nevertheless, the Al-centroid distance  $d_{\text{Al–X}}$  decreases going from the anionic complex to the cationic one ( $d_{\text{Al–X}}$ =2.276, 1.978, 1.804 Å

respectively). This reflects the evolution of the complexation which becomes stronger in the cation compared to the two others.

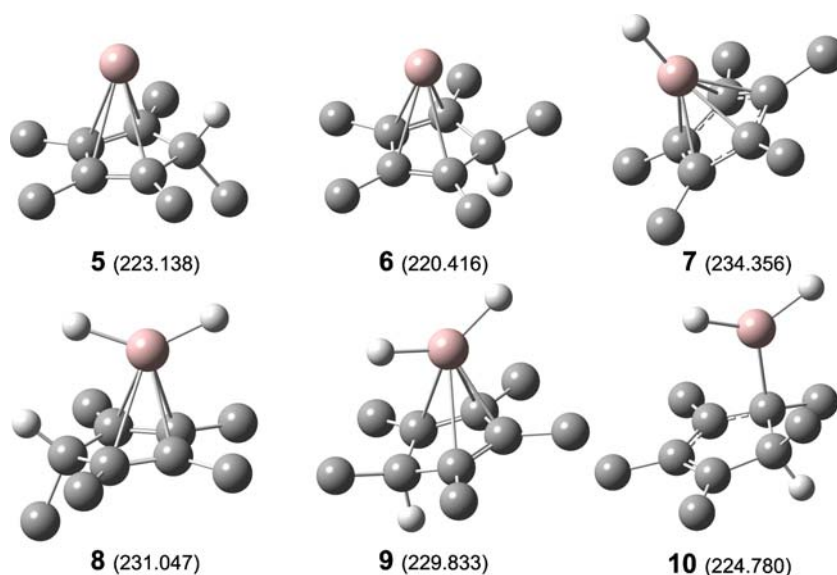
On the other hand, let's take a look at the charge-transfer from the Cp ligands toward the deficient  $\text{Al}_2\text{H}_3$ . Here again, the maximum is observed for the cationic compound. Both the strong Lewis-acid properties of  $\text{Al}_2\text{H}_3$  and the Cp charge wealth (Lewis-base), favor this transfer especially for neutral and cationic complexes (0.989 and 1.397e respectively).

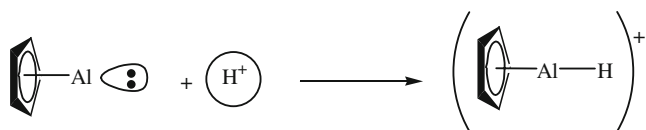
Finally, we have examined the di and monobridged sandwiched  $\text{Al}_2\text{H}_3$  by tilting one or two bridged hydrogen atoms respectively from **1**. The optimization on the total PES starting from both structures led to **4** which has the  $\text{C}_2$  symmetry and one bridged hydrogen (Fig. 1). The energetic deviation from the tribridged arrangement is about 4 kcal mol<sup>-1</sup>. Nevertheless, as the calculations are done in gas-phase conditions, we performed others in condensed phase using the Tomasi model [36–38], taking into account the solvent effect. The results support strongly the tribridged arrangement **1**. For example, this later becomes 11 kcal mol<sup>-1</sup> lower than **4** when the THF parameters are considered in the calculations. We can thus conclude, that the tribridged structure  $\text{Cp}^*\text{Al}(\mu\text{-H})_3\text{AlCp}^*$  is favored in condensed phases.



As we have mentioned in the introduction, in spite of their short lifetime,  $\text{Cp}^*\text{AlH}_2$  and  $\text{Cp}^*\text{Al}$  have been experimentally observed and structurally characterized [19]. Knowing that the corresponding dimers  $[\text{Cp}^*\text{Al}]_2$

**Fig. 4** Protonated structures of  $\text{CpAl}$  (**5**, **6** and **7**) and  $\text{Cp}^*\text{AlH}_2$  (**8**, **9** and **10**) with protonation energies (kcal mol<sup>-1</sup>) calculated as :  $[\text{E}(\text{i})-\text{E}(\text{AlCp}^*)]$ , ( $\text{i}=\mathbf{5}$ , **6** and **7**); and  $[\text{E}(\text{j})-\text{E}(\text{H}_2\text{AlCp}^*)]$ , ( $\text{j}=\mathbf{8}$ , **9** and **10**). To compare these values we discuss them without negative sign. The hydrogen atoms of methyl groups are omitted for clarity





**Scheme 1** Strong Orbital Interaction between no-bonding  $p$  of aluminum and empty  $s$  of the proton

and  $[\text{Cp}^*\text{AlH}_2]_2$  have not been experimentally observed, we suggest that **2** and **3** monomers can interact with each other in an acidic medium yielding the expected  $[\text{Cp}^*\text{Al}(\mu\text{-H})_3\text{AlCp}^*]^+$  complex. This raises two important questions that need experimental testing: can either  $\text{Cp}^*\text{Al}$  or  $\text{Cp}^*\text{AlH}_2$  be protonated? If so, can the protonated form react with the neutral one, leading to  $[\text{Cp}^*\text{AlH}_3\text{Cp}^*]^+$  compound? In order to get an answer to these questions, we studied  $\text{Cp}^*\text{AlH}_2$ ,  $\text{Cp}^*\text{Al}$  and their corresponding protonated forms  $\text{Cp}^*\text{AlH}_3^+$  and  $\text{Cp}^*\text{AlH}^+$ .

In order to gain computation time and memory space, initially we modeled the  $\text{Cp}^*$  ligands by Cp (H atoms instead of methyls) but the  $\eta^5$  hapticity in  $\text{CpAlH}_2$  seems to be favored by steric-effect of methyl groups since a fluxional phenomena has been observed between  $(\eta^2\text{-Cp})\text{AlH}_2$  and  $(\eta^3\text{-Cp})\text{AlH}_2$  minima *via*  $(\eta^5\text{-Cp})\text{Al}$  transition-state (see [supplementary material](#)). To avoid any inaccurate interpretation, we abandoned this modelization and realized our study with  $\text{C}_5(\text{Me})_5$  ligands.

In accordance with the experimental results, both  $\text{Cp}^*\text{Al}$  and  $\text{Cp}^*\text{AlH}_2$  adopt the same structures,  $C_{5v}$  and  $C_s$  respectively with Al atom in the  $C_5$  axis of the ring (Fig. 3) although the final optimizations was done on the total PES (without geometrical restrictions).

$\text{Cp}^*\text{Al}$  has been presented, in previous works, as a Lewis-base with the lone pair on the aluminum atom [42–45]. However, the protonation has been considered as well on Al atom as on the cyclopentadienyl since there is a high electron content. In Fig. 4 we present all stationary points and the corresponding protonation energies of  $\text{Cp}^*\text{Al}$  and  $\text{Cp}^*\text{AlH}_2$ . As we can see, the protonation on aluminum atom could occur only for **2** yielding  $[\text{Cp}^*\text{AlH}]^+$  (**7**). This is ensured by the  $s$ - $p$  hybridized orbital of Al atom which can constitute a target for  $\text{H}^+$  attack (Scheme 1). For  $\text{Cp}^*\text{AlH}_2$ , the protonation on the aluminum with  $\eta^5\text{-Cp}^*$  is not a minimum on the total PES. This is due to the total involvement of the  $s$  and the three  $p$  atomic orbitals of the metal in the ring-metal and metal-hydrogen binding. Consequently, the protonation cannot occur on the Al center for  $\text{Cp}^*\text{AlH}_2$ .

Concerning the proton attack on the  $\pi$  system of the cyclopentadienyl, a covalent bond C-H is formed leading to a reduction of the ring hapticity toward the metal atom (Fig. 4). This is slightly disfavored with regard to the Al protonation. The corresponding energetic deviation ( $E_p(\mathbf{7}) - E_p(\mathbf{8})$  is  $3,31 \text{ kcal mol}^{-1}$ ) in the gas phase, and becomes

$5.484, 6.039, 5.150, 5.906 \text{ kcal mol}^{-1}$  while taking into account the solvent effects (THF,  $\text{H}_2\text{O}$ , diethyl ether, and ethanol respectively).

Therefore, we can advance that the  $[\text{Cp}^*_2\text{Al}_2\text{H}_3]^+$  formation could result from an interaction between the protonated  $\text{Cp}^*\text{AlH}^+$  and the neutral  $\text{Cp}^*\text{AlH}_2$ . This interaction is supported by the energetic stabilization ( $\Delta E = E(\text{complex}) - E(\text{Cp}^*\text{AlH}^+) - E(\text{Cp}^*\text{AlH}_2)$ ) which is about  $22 \text{ kcal mol}^{-1}$  (Table 1). In the case of the model  $\text{CpAl}(\mu\text{-H})_3\text{AlCp}$ , such stability is about 20., 29. and  $30. \text{ kcal mol}^{-1}$  at B3LYP/6-311+g(d,p), MP4/6-31G(d,p)//B3LYP/6-31G(d,p) and CCSD(T)/6-31G(d,p)//B3LYP/6-31G(d,p) levels respectively (Table 2).

## Conclusions

In this work we attempted to identify factors that might stabilize the metallocene complex  $(\eta^5\text{-Cp}^*)\text{Al}(\mu\text{-H})_3\text{Al}(\eta^5\text{-Cp}^*)$ , where the tribridged  $\text{Al}_2\text{H}_3$  entity is sandwiched between two  $\text{Cp}^*$  ligands. However, in addition to its bonding vacant orbitals extended on  $p_z$  and  $s$  atomic orbitals of both Al and H atoms,  $\text{Al}_2\text{H}_3$  mono, double or triple cation implies its antibonding orbitals combinations to interact with the in-phase and the out-of-phase mixtures of the three highest occupied MOs of  $[\text{Cp}\dots\text{Cp}]^{2-}$  fragment. On the other hand, the  $\text{Cp}^*\text{AlH}_2$  and the  $\text{Cp}^*\text{Al}$  which have been experimentally observed could interact in acidic medium ( $[\text{Cp}^*\text{AlH}]^+$  and  $\text{Cp}^*\text{AlH}_2$  reactant) to form the  $[\text{Cp}^*_2\text{Al}_2\text{H}_3]^+$  complex. These, enable us to conclude that the tri- $\mu$ -hydrido-bis $[(\eta^5\text{-C}_5\text{Me}_5)\text{aluminum(III)}]$  has all the assets to be part of a reactions' sequence, at least as an intermediate, if not as a final product.

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