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Sandwich-like Compounds Based on the All-Metal Aromatic Unit Al_4^{2-} and the Main-Group Metals M (M = Li, Na, K, Be, Mg, Ca)

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Abstract: Inspired by the pioneering experimental characterisation of the all-metal aromatic unit Al_4^{2-} in the bimetallic molecules MAl_4^- (M = Li, Na, Cu) and by the very recent theoretical design of sandwich-type transition-metal complexes $[Al_4MAl_4]^{q-}$ ($q=0$–2; M = Ti, V, Cr, Zr, Nb, Mo, Hf, Ta, W), we used density functional theory (DFT) calculations (B3LYP/6-311+G(d) to design a series of novel non-transition-metal sandwich complexes based on the all-metal aromatic unit Al_4^{2-} and the main-group metals M (M = Li, Na, K, Be, Mg, Ca). The traditional *homo-decked sandwich* compounds $[Al_4MAl_4]^{q-}$ (without counterions) and $(n\mathrm{M})^{q+}[Al_4MAl_4]^{q-}$ (with counterions M) ($q=2$–3, M = Li, Na, K, Be, Mg, Ca), although some of them are truly energy minima, have a much higher energy than many fused isomers. We thus concluded that it seems unlikely for Al_4^{2-} to sandwich the main-group metal atoms in the *homo-decked sandwich* form. Alternatively, we proposed a new type of sandwich complex, namely *hetero-decked sandwich* compounds $[CpMAl_4]^{q-}$, that are the ground-state structures for each M both with and without counterions. It was shown that with the rigid Cp^- partner, the all-metal aromatic unit Al_4^{2-} might indeed act as a "superatom". These new types of all-metal aromatic unit-based sandwich complexes await future experimental verification.

Keywords: all-metal aromaticity · aluminum · density functional calculations · main-group metals · sandwich complexes

Introduction

Aromaticity is one of the most useful concepts in chemistry for predicting and understanding the stability and other unique properties of molecules. In general, aromaticity has been limited to hydrocarbon and heterocyclic systems with $4n+2$ electrons. However, the unexpected observation of the square-planar Al_4^{2-} unit in bimetallic compounds MAl_4^- (M = Li, Na, Cu) by Li et al in 2001 has extended the concept of "aromaticity" to certain all-metal species.[1] Many such aromatic species, for example XAl_3^- (X = Si, Ge, Sn, Pb),[2] M_4^{2-} (M = Ga, In, Tl, Sb, Bi),[3,4] M_4^{2+} (M = Se, Te),[5] M_3^- (M = Al, Ga),[6] Al_6^{2-},[6f] Hg_4^{6-},[7] M_5^{6-} (M = Ge, Sn, Pb),[8] M_5^- (M = Sb, Bi),[9] Au_5Zn^+,[10a] Cu_3^{3+},[10b] Cu_4^{2-}?[10c] $[Fe(X_5)]^+$ (X = Sb, Bi),[11] etc., have since been added to the growing all-metal aromatic family.[12] These species are usually electron-deficient and possess large resonance-stabilisation energies, which is ascribed to the "multiple aromaticity" feature.[13] Because of their interesting chemical structures, bonding properties and potential applications in materials science, it is not surprising that the all-metal aromatic species have received considerable attention.[12] Interestingly, some species (e.g. Al_3^- and Hg_4^{6-}) were identified experimentally before the Al_4^{2-} milestone. In particular, Hg_4^{6-} already existed in ancient amalgams![7] It is thus reasonable to state that the all-metal aromatic molecules have and would continue to play an important role in novel materials science.

Now that many all-metal aromatic units have been experimentally confirmed, one goal is to design novel one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) cluster-assembled materials based on the concept of "all-metal aromaticity". Ritter has stated,[1b] "···these compounds eventually could be useful building blocks in complex semiconducting or superconducting materials", whereas Kuznetsov et al. stated,[6f] "···the question remains if the X_4^{2-} aromatic rings can be incorporated into sandwich-type complexes···" (X = Al, Ga, In). We feel that such issues should also exit for the assembly of other all-metal aromatic

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Supporting information for this article (energy profiles of the various structures for homo-, hetero- and multi-decked species) is available on the WWW under http://www.chemeurj.org/ or from the author.

species. Fortunately, for the milestone molecule Al_4^{2-}, theoretical efforts have been undertaken very recently to design potential sandwich-like complexes in two excellent papers published by the group of Mercero and Ugalde.[14a,b] They successfully located a series of sandwich-like compounds $[Al_4MAl_4]^{q-}$ ($q=0$–2, M = Ti, V, Cr, Zr, Nb, Mo, Hf, Ta, W) as energy minima based on DFT calculations. These compounds have a nearly perfect square-planar Al_4 structure, large dissociation energies and comparable nucleus-independent chemical shift (NICS) values to free Al_4^{2-}. Thus, it was concluded that the aromatic nature of the square Al_4^{2-} species remains intact upon complexation by transition metals.

The pioneering work of Mercero, Ugalde, and co-workers[14a,b] demonstrated that the all-metal aromatic Al_4^{2-} deck could be used to sandwich the transition-metal atoms that have partially unoccupied d orbitals. An analysis of their orbitals indicates that the d orbitals play an important role in the interaction of M with Al_4^{2-} decks. However, whether or not the Al_4^{2-} deck can be used to sandwich the main-group metal atoms (the d orbitals are fully occupied or completely vacant) is completely unknown. Also, alkali metals and alkaline-earth metals are highly electropositive and the Al_4 ring is highly electron-deficient. Such a donor–acceptor interaction could lead to one-dimensional chain-like polymeric materials.[15] Moreover, the effective charge transfer between the metal atom and the Al_4 ring may possibly induce unique higher-order non-linear optical (NLO) properties.[16] We are aware that the well-known cyclopentadienyl anion (Cp^-) can sandwich almost all the elements in the periodic table (transition-metal, main-group metal, rare-earth metal and non-metal types). The versatility of Cp^- has led to a rich field of metallocene chemistry.[17a] To inspect the versatility of the novel and exotic Al_4^{2-} deck, it is highly desirable to study the sandwich-like complexes based on non-transition-metal atoms such as alkali metals and alkaline-earth metals.

Herein, we designed a series of non-transition-metal sandwich complexes based on the all-metal aromatic unit Al_4^{2-} and the main-group metals M (M = Li, Na, K, Be, Mg, Ca) by means of density functional theory (DFT) calculations (B3LYP/6-311+G(d)). The traditional *homo-decked sandwich* compounds $[Al_4MAl_4]^{q-}$ (without counterions) and $(nM)^{q+}[Al_4MAl_4]^{q-}$ (with counterions M) ($q=2$–3, M = Li, Na, K, Be, Mg, Ca) are energetically much high-lying than many fused isomers, although some of them are truly energy minima. We thus concluded that it seems unlikely for Al_4^{2-} to sandwich the main-group metal atoms in the *homo-decked sandwich* form. Alternatively, we proposed a new type of sandwich complexes, namely, *hetero-decked sandwich* compounds $[CpMAl_4]^{q-}$, that are the ground-state structures for each M both with and without counterions. It was shown that in conjunction with the rigid Cp^- partner, the all-metal aromatic unit Al_4^{2-} might indeed act as a "superatom".[18] The new types of all-metal sandwich complexes based on an aromatic unit await future experimental verification.

Computational Methods

Initially, we fully optimised the geometries of $[DAl_4M]^{q-}$ ($D = Al_4^{2-}$, Cp^-; M = Li, Na, K, Be, Mg, Ca) by employing analytical gradients with a polarised split-valence basis set (6-311+G(d))[19] and the hybrid method, which includes a mixture of Hartree–Fock exchange with density functional exchange correlation (B3LYP),[20] as implemented in Gaussian 03.[21] After geometrical optimisation, normal mode vibrational analysis was performed to check whether the obtained structure is a true minimum point with all real frequencies or a first-order transition state with only one imaginary frequency. Despite its widespread use, aromaticity is more a concept rather than a directly measurable quantity. Consequently, measurements of aromaticity rely on many diverse criteria.[22] Among them, the nucleus-independent chemical shift (NICS), based on the "absolute magnetic shielding" taken at the centre of a ring compound, is widely used and has been proven to be accurate for ordinary cyclic carbon compounds.[23] Recently, the method has also been successfully used for inorganic cyclic aromatic compounds,[24] including characterisation of the so-called d-orbital aromaticity.[25] Thus, the NICS values were also calculated at the B3LYP/6-311+G(d) level of theory. A positive value of the NICS indicates that the molecule is anti-aromatic, a negative value indicates the aromaticity of the molecule. The NICS calculated at the centre of the square (NICS(0)) describes the σ aromaticity and a NICS greater than 1 Å out of the square plane (NICS(1)) describes the π aromaticity of the molecule. All calculations were performed with the Gaussian 03 program.[21]

Results and Discussion

$[Al_4MAl_4]^{q-}$: As model calculations, we first investigated the assembly of the Al_4^{2-} unit in the traditional "homo-decked sandwich" form, $[Al_4MAl_4]^{q-}$ with M = Li, Na, K, $q=3$; M = Be, Mg, Ca, $q=2$, at the B3LYP/6-311+G(d) level. The possible types of sandwich are shown in Figure 1. The type **I** structure is similar to the well-known metallocene CpMCp, in which two Cp^- units adopt a face–face (f–f) configuration. After a detailed structural search at the B3LYP/6-311+G(d) level, we obtained seven sandwich forms as energy minima with all-real frequencies. The

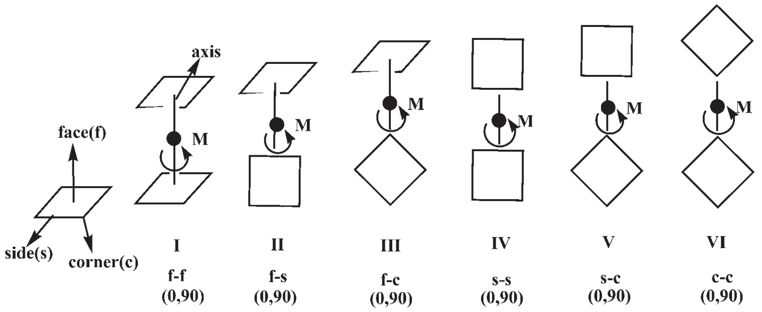

Figure 1. Six (**I**–**VI**) possible types of $[Al_4MAl_4]^{q-}$ sandwiches for each M. In each type, one unit can rotate along the axis by 0° and 90°.

energy profiles of the most relevant $[C_2Al_8M]^{q-}$ species, that is, all sandwich forms and those with a lower energy than the lowest-energy sandwich form, are shown schematically in Figure 2. The other isomers are given in the Supporting Information. Firstly, all the face–face (f–f) type traditional sandwich forms are not minima, which is in contrast to metallocenes. Secondly, for all the six main-group elements, the sandwich species **IV**, **V** and **VI** have very similar energies and are all energetically lower than **I**, **II** and **III**. Structures **I**–**III** can be easily converted to the lower-energy **IV**–**VI** structures by rotation of the Al_4^{2-} deck along different axes. The interconversion between **IV**–**VI** by a simple rotation is also very easy, as indicated by the small rotational frequency. Thirdly, for all six metals, the lowest-energy sandwich structure is not the global minimum point; the ground-state isomers are fusion isomers that lie 24.79, 24.90, 30.96, 51.00, 31.06 and 24.80 kcal mol^{-1}, respectively, lower than the sandwich forms.

Saturated compounds: $(n\mathrm{M})^{q+}[\mathrm{Al_4MAl_4}]^{q-}$ and the effect of the counterions: The sandwich forms $[Al_4MAl_4]^{q-}$ ($q=2$ and 3) considered above are negatively charged. Neutral species in the form of a salt are preferable if they are to be synthesised. We thus investigated $(n\mathrm{M})^{q+}[\mathrm{Al_4MAl_4}]^{q-}$ (M = Li, Na, K, $q=3$, $n=3$; M = Be, Mg, Ca, $q=2$, $n=1$). To systemically consider and investigate all the various saturated compounds, we considered the insertion, addition and bridged forms, from face, side, corner and combined coordination directions based on model compounds. Figure 3 depicts all the neutral sandwich forms and the lowest-energy non-sandwich isomer that has lower-energy than the lowest-energy sandwich form. The other non-sandwich isomers are given in the Supporting Information. For simplicity, we only use ^{1}**1**(f-f-0) D_{4h} as the reference energy for M = Li, Na, K and ^{1}**1**(f-f-0) D_{4h} as the reference energy for M = Be, Mg, Ca, although they are not energy minima. We are aware that for all six metals M = Li, Na, K, Be, Mg and Ca, all sandwich forms are not energy minima, except for Ca, ^{1}**1**(s-c) (−47.31) and ^{1}**1**(c-c) (−46.35) are minima. Compared with many fusion isomers, the only two minima of the sandwich-like compounds have a high energy. For all six metals M = Li, Na, K, Be, Mg and Ca, many fused isomers have lower energies than the sandwich structures. We can conclude that it seems unlikely that Al_4^{2-} sandwiches the main-group metal atoms in the homo-decked sandwich form. Additionally, the counterions still introduce an electrostatic stabilisation. One cannot deduce the salt structure of the Al_4^{2-}-based homo-decked sandwich complex simply from the charged model. Consideration of the charge-compensated species is indispensable! However, such a feature has not been revealed in previous studies on metallocenes (such as the traditional CpMCp^{q-}[17a] and the novel $P_5MP_5^{q-}$,[14c–e] $N_4MN_4^{q-}$[14f–i] and $Al_4MAl_4^{2-}$[14a–b]).

Our results on the assembly of two Al_4^{2-} units are in good agreement with the concerns expressed by Seo and Corbett in a mini-review[1c] of the work of Li et al. Therefore, the challenge would be to have the M_4^{2-} units (Al_4^{2-} and its analogues) completely separated from each other because an incomplete separation may lead to fusion of the M_4^{2-} building blocks to form larger clusters. Additionally, fusion of the two-dimensional all-metal aromatic Al_3^{-} units has been considered to result in the three-dimensional all-metal aromatic Al_6^{2-} unit. This unit has been experimentally characterised by photoelectron spectroscopy as bimetallic molecules MAl_6^{-} (M = Li, Na, K, Cu, and Au).[6f]

$[\mathrm{CpMAl_4}]^{q-}$: The above "discouraging" results prompted us to readdress the question: "How can the all-metal aromatic unit Al_4^{2-} sandwich the main-group metal atoms to form the assembled molecular materials?" We are aware that the organic aromatic species *cyclo*-$C_5H_5^{-}$ (Cp^{-}) is a very well-known and versatile unit with respect to sandwiching various atoms and has led to a rich chemistry of mononuclear metallocenes (CpMCp).[17a] Very recently, the Cp^{-} pairs were even found to sandwich a direct Zn−Zn bond to form the first stable Zn−Zn-bonded species $CpZn_2Cp$, which is also the first dinuclear metallocene.[17b–c] This indicates that Cp^{-} is a powerful sandwich deck. We were thus prompted to wonder whether the all-metal aromatic deck Al_4^{2-} can cooperate with the organic aromatic deck Cp^{-} to sandwich metal atoms. Luckily, this is indeed the case!

We propose a new "hetero-decked sandwich" for the assembly of the all-metal aromatic units into molecular materials: metal (M) atoms are sandwiched by different decks as DMD* units (D, D* = sandwich decks). By taking advantage of the high stability of Cp^{-}, a new class of sandwich compounds $[\mathrm{CpMAl_4}]^{q-}$ can be designed. Such compounds are obviously of special interest because they contain both the classic organic aromatic unit Cp^{-} and the novel, all-metal aromatic unit Al_4^{2-}. The six energy profiles of M = Li, Na, K, Be, Mg, Ca are shown in Figure 2a–g, respectively. In contrast to the homo-decked sandwich scheme, the ground-state structure is the sandwich isomer **Het-M1** that has two types of sandwich forms, namely, face–face (f–f) and face–side (f–s). The first "face" means the plane of Cp^{-}, while the second "face" and "side" mean the plane and one Al−Al bond of Al_4^{2-}, respectively. "**Het**" stands for the "hetero Cp^{-} and Al_4^{2-} decks". At the B3LYP/6-311+G(d) level, the (f–f) form is more stable, except for M = Li and Na for which the (f–s) form is lower than the (f–f) form by 2.36 and 0.94 kcal mol^{-1}, respectively. The energy of the interconversion transition **Het-Mtsa** lies close to that of **Het-M1(f–f)**. The facile **Het-M1(f–f)**↔**Het-M1(f–s)** transformation process can be simplistically viewed as the opening↔closure of the Al_4^{2-} deck above the "ground" deck Cp^{-}. The rearrangement of the sandwich form **Het-M1** to other high-energy isomers is generally difficult with considerable barriers. Thus, the **Het-M1** is the ground-state sandwich isomer.

Among all the considered $[\mathrm{CpAl_4M}]^{q-}$ systems, the planar Cp^{-} structure is well maintained, indicative of the unique "rigidity" of this organic unit. Fusion of the Cp^{-} and Al_4^{2-} decks to form new C−Al or C−M bonds is energetically unfavourable, in sharp contrast to the situation for the $[Al_8M]^{q-}$ systems. This results in the high stability of the

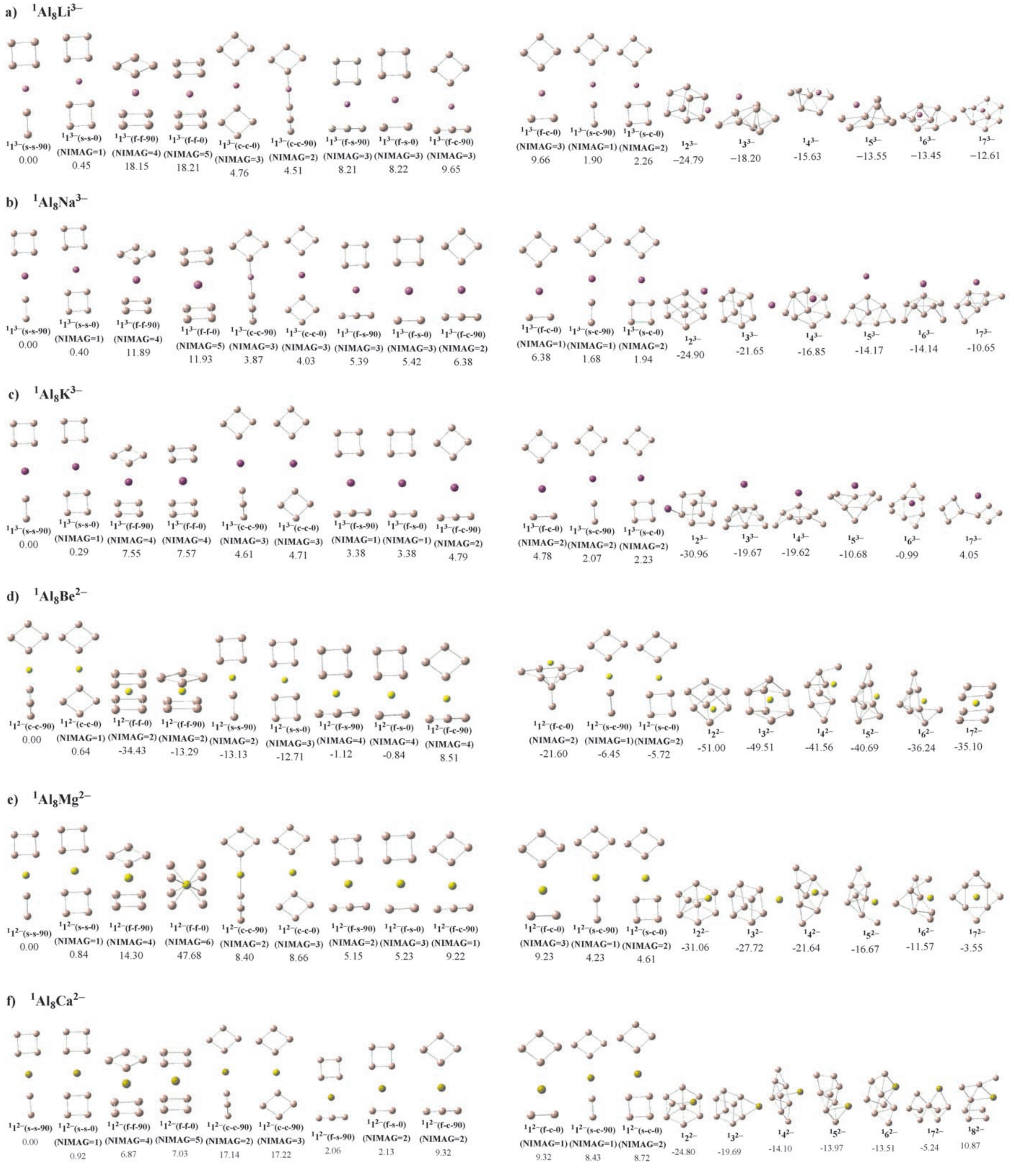

Figure 2. Schematic energy profile for singlet $^{1}[Al_8M]^{q-}$: a) (M,q) = (Li,3); b) (M,q) = (Na,3); c) (M,q) = (K,3); d) (M,q) = (Be,2); e) (M,q) = (Mg,2); f) (M,q) = (Ca,2) calculated at the B3LYP/6-311+G(d) level. Energy values are in kcal mol^{-1}. Color code: orange Al; black C; white H; purple Li, Na, and K in a), b) and c) respectively; yellow Be, Mg, Ca in d) e) and f), respectively. Where "NIMAG" is the number of the imaginary frequency of saddle point. $^{m}N^{q-}$: where "m" is the spin electron state, "N" is the sequence number of the various isomers and superscript "$q-$" is the charge of the total system. For simplicity, the notations "Ho-Li", "Ho-Na" "Ho-K" "Ho-Be" "Ho-Mg" and "Ho-Ca" for isomers are omitted, and we only listed the sandwich-like and low-lying isomers, all the other isomers are found in the Supporting Information. It should be pointed out that the representations of $^{1}1^{2-}$-(f-f-0), $^{1}1^{2-}$(f-f-90), and $^{1}1^{2-}$(f-c-0) for M = Be only formally represent the initial sandwich-type forms before geometry optimisation, although they are fused isomers after geometry optimisation. This also applies to M = Mg, $^{1}1^{2-}$(f-f-0).

Figure 3. Most relevant species of Al_8M_4 (M = Li, Na, K) and Al_8M_2 (M = Be, Mg, Ca) at the B3LYP/6-311+G(d) level. Energy values are in kcal mol^{-1}. For definitions see Figure 2. Color code: orange Al; black C; white H; purple Li, Na, and K in a), b) and c) respectively; yellow Be, Mg, Ca in d) e) and f), respectively. It should be pointed out that the representations of Al_4Li_4 (^{1}1(f-f-0), NIMAG = 4, 0.00) only formally represents the initial sandwich-type forms (two Al_4-decks are separated by four Li-atoms before geometry optimization), although they are fusion isomers after optimisation. Here, we only use it as energy reference.

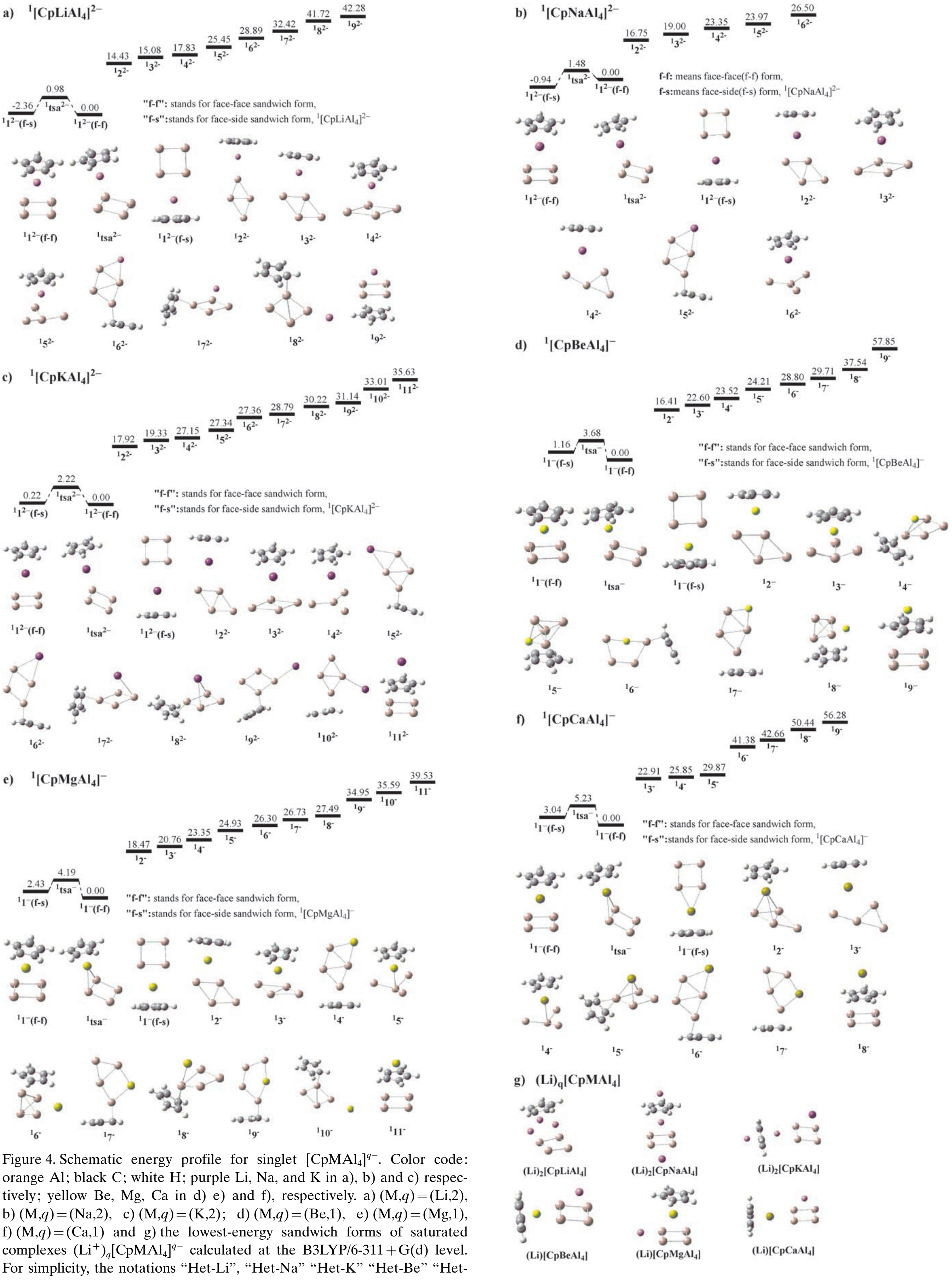

Figure 4. Schematic energy profile for singlet [CpMAl$_4$]$^{q-}$. Color code: orange Al; black C; white H; purple Li, Na, and K in a), b) and c) respectively; yellow Be, Mg, Ca in d) e) and f), respectively. a) (M,q) = (Li,2), b) (M,q) = (Na,2), c) (M,q) = (K,2); d) (M,q) = (Be,1), e) (M,q) = (Mg,1), f) (M,q) = (Ca,1) and g) the lowest-energy sandwich forms of saturated complexes (Li$^+$)$_q$[CpMAl$_4$]$^{q-}$ calculated at the B3LYP/6-311+G(d) level. For simplicity, the notations "Het-Li", "Het-Na" "Het-K" "Het-Be" "Het-Mg" and "Het-Ca" for isomers are omitted. Energy values are in kcal mol^{-1}.

hetero-decked sandwich complexes $[CpAl_4M]^{q-}$. Thus, the rigid organic deck Cp^- can effectively assist the all-metal aromatic deck Al_4^{2-} to sandwich metal atoms. The "hetero-decked sandwich" scheme can stabilise the Al_4^{2-} unit by avoiding fusion. In contrast to the traditional homo-decked sandwich scheme, the present "hetero-decked sandwich" scheme can effectively incorporate the Al_4^{2-} unit into the assembled molecular compounds to produce a new type of metallocene.

Saturated compounds: $(Li^+)_q[CpMAl_4]^{q-}$ and the effect of counterions: The above-considered sandwich forms $[CpMAl_4]^{q-}$ (M = Li, Na, K, $q=2$; M = Be, Mg, Ca, $q=1$) have a single or a double negative charge. For the purpose of actual synthesis, neutral species in the form of a salt are preferable. We thus investigated the properties of $(Li^+)_q$-$[CpMAl_4]^{q-}$. For each M, various isomeric forms are considered at the B3LYP/6-311+G(d) level. For each M, the lowest-lying sandwich isomer in charged $[CpMAl_4]^{q-}$ is also the lowest-lying structure for neutral $(Li^+)_q[CpMAl_4]^{q-}$. Indeed, the counterions have little influence on the nature of the low-lying structures. This is similar to the situation with respect to the effects of counterions of traditional metallocenes. For simplicity, we only show the low-lying sandwich species in Figure 4g. The other higher-energy sandwich forms and other isomers are given in the Supporting Information.

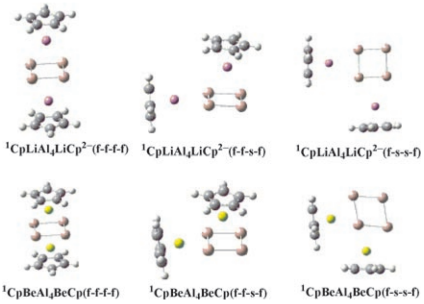

Figure 5. Illustrative structures of extended sandwich complexes $[Cp_2Al_4M_2]^{q-}$ [(M = Li, $q=1$); (M = Be, $q=0$)] calculated at the B3LYP/6-311+G(d) level. Color code: orange Al; black C; white H; purple Li; yellow Be.

Table 2. The ground states of saturated sandwich compounds (see Figure 4g.) $(Li)_q[CpMAl_4]$ ($q=2$, M = Li, Na, K; $q=1$, M = Be, Mg, Ca) calculated at the B3LYP/6-311+G(d) level.

	$(Li)_q[CpMAl_4]$	Dihedral angle (Al-Al-Al-Al) [°]	Al−Al bond length [Å]
Li	$(Li)_2[CpLiAl_4]$	0.037	2.6375, 2.5124, 2.5583, 2.5128
Na	$(Li)_2[CpNaAl_4]$	0.040	2.6154, 2.6135, 2.6162, 2.6171
K	$(Li)_2[CpKAl_4]$	0.080	2.6193, 2.5420, 2.5798, 2.5408
Be	$(Li)[CpBeAl_4]$	0.047	2.6131, 2.5264, 2.6052, 2.5273
Mg	$(Li)[CpMgAl_4]$	0.052	2.6558, 2.5349, 2.5860, 2.5345
Ca	$(Li)[CpCaAl_4]$	0.013	2.6499, 2.5240, 2.5700, 2.5238

Extended sandwich structures: –$CpMAl_4M\cdots Cp$– based on Al_4^{2-}: Some metallocenes are already known to form extended sandwich complexes.[17a] As an extension of the present study, we further designed the extended systems that contain more than one Cp^- unit in various sandwich forms at the B3LYP/6-311+G(d) level. For simplicity, only selected species with the lowest energy are shown in Figure 5 (M = Li and Be), while many others are given in the Supporting Information. $CpBeAl_4BeCp$ with a Cp^- terminus is 37.59 kcal mol^{-1} more stable than its $CpBeCpBeAl_4$ isomer with a Al_4^{2-} terminus. This stability arises from the effective avoidance of fusion between the sandwiching decks owing to the unique rigidity of Cp^-. Moreover, in this type of multi-hetero-decked sandwich form, the opening/closing process of the Al_4^{2-} deck should be greatly suppressed. We thus proposed the promising supermolecular chains to be $Cp(MAl_4MCp)_n$ with a Cp^- terminus. Yet, as expected, the multi-hetero-decked sandwich form $[Al_4BeCpBeAl_4]^-$ with a Al_4^{2-} terminus is less stable by 25.21 kcal mol^{-1} than the Al_4-fused form $[BeCpBeAl_8]^-$ at the B3LYP/6-311+G(d) level.

In general, the square planarity (see Tables 1 and 2) and orbital features of the all-metal aromatic unit Al_4^{2-} are well maintained during cluster assembly, for example, the tri-hetero-decked sandwich form $CpMAl_4MCp^{q-}$ (M = Li and Be). Figure 6 illustrates the selected orbital diagrams[27] of $CpLiAl_4LiCp^{2-}$ and $CpBeAl_4BeCp$ as well as the comparative species Al_4^{2-}. We can see that the three characteristic orbitals in the free Al_4^{2-} (one delocalized π (HOMO), two delocalized σ (HOMO-1 and HOMO-2)) which contribute to the so-called "multiple aromaticity", can be found in both multi-hetero-decked sandwich compounds $[CpLiAl_4LiCp]^{2-}$ and $CpBeAl_4BeCp$. A significant difference is that the HOMO orbital in the free Al_4^{2-} is moved to HOMO-2 and HOMO-3 in $[CpLiAl_4LiCp]^{2-}$ and $CpBeAl_4BeCp$, respec-

Table 1. The molecular properties of the Al_4 units in all of the sandwich forms (face–face (f–f) and face–side (f–s)) of $[CpMAl_4]^{q-}$ calculated at the B3LYP/6-311+G(d) level.

M	$[CpMAl_4]^{q-}$	Dihedral angle (Al-Al-Al-Al) [°]		Al−Al bond length [Å]	
		f–f	f–s	face–face(f–f)	face–side(f–s)
Li	$^1[CpLiAl_4]^{2-}$	0.012	0.014	2.5841, 2.5795, 2.5821, 2.5867	2.5902, 2.5614, 2.5794, 2.5618
Na	$^1[CpNaAl_4]^{2-}$	0.018	0.003	2.5857, 2.5840, 2.5850, 2.5865	2.6049, 2.5549, 2.5753, 2.5551
K	$^1[CpKAl_4]^{2-}$	0.001	0.006	2.5869, 2.5864, 2.5867, 2.5872	2.6034, 2.5615, 2.5754, 2.5616
Be	$^1[CpBeAl_4]^-$	0.245	0.006	2.5819, 2.5565, 2.5697, 2.5970	2.5914, 2.5079, 2.5634, 2.5058
Mg	$^1[CpMgAl_4]^-$	0.002	0.012	2.5984, 2.5873, 2.5958, 2.6078	2.6441, 2.4954, 2.5567, 2.4960
Ca	$^1[CpCaAl_4]^-$	0.060	0.003	2.5872, 2.5878, 2.5872, 2.5864	2.6261, 2.5085, 2.5476, 2.5084

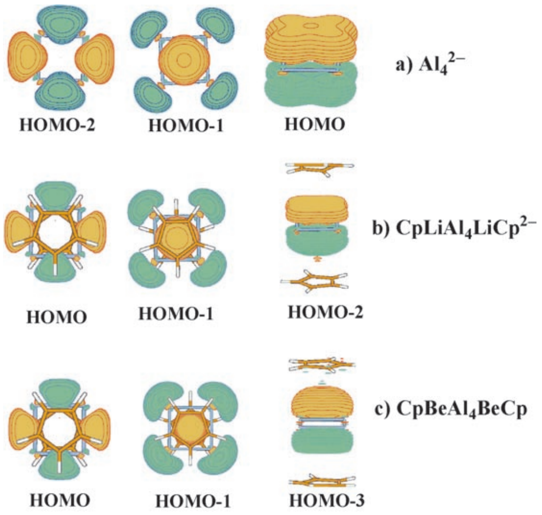

Figure 6. Characteristic orbital diagrams[27] of a) Al_4^{2-}, b) $[CpLiAl^4LiCp]^{2-}$ and c) $CpBeAl_4BeCp$.

tively. Thus, the delocalised π orbital is greatly stabilised upon hetero-decked sandwiching.

We particularly note that for all the six main-group metals M = Li, Na, K, Be, Mg and Ca, both the face–face (f–f) forms **Het-M1(f–f)** and the face–side (f–s) forms **Het-M1(f–s)** possess a square-like Al_4^{2-} structure (Table 1). We have calculated the NICS values of the aromatic squares at different points around the Al_4 rings before and after the metallocene-like molecules are formed. One of the most remarkable properties of the Al_4^{2-} ring is its multiple aromaticity,[13] as revealed by the negative values of both NICS(0) and NICS(1) (Table 3). Once the ring interacts with the main-group metal to form the sandwich complex, the Al_4^{2-} ring maintains its multiple aromaticity (see NICS(0) and NICS(1) values in Table 3). We conclude that the Al_4^{2-} ring does indeed maintain its aromaticity upon complex formation. Thus, it is fair to say that the complexes have an all-metal aromatic-metal-organic aromatic structure.

Implications: Herein we have described attempts to design sandwich complexes based on an all-metal aromatic unit Al_4^{2-} and a main-group metal (M = Li, Na, K, Be, Mg, Ca). Our work differs from that on the transition-metal sandwich compounds $[Al_4MAl_4]^{q-}$ (q = 0–2, M = Ti, V, Cr, Zr, Nb, Mo, Hf, Ta, W) very recently designed by Mercero, Ugalde, and co-workers.[14a–b] Firstly, we systematically considered various types of sandwich beyond the traditional face–face (f–f) sandwich form, which was only considered in previous work.[14] Secondly, we considered the fusion stability of such systems and searched for various fusion isomers. Thirdly, the hetero-decked sandwich scheme was introduced for the first time for the assembly of the all-metal aromatic Al_4^{2-} into molecular materials. Fourthly, we have shown that in our newly proposed hetero-decked sandwich scheme, the all-metal aromatic Al_4 deck could be used to sandwich not only the transition metal,[26] but also a main-group metal. Thus the versatility of the Al_4 deck in forming the hetero-decked sandwich complexes is clearly manifested.

More interestingly, as in the work of Kuznetsov et al,[6f] the fusion of two 2D all-metal aromatic Al_3^- units can lead to the 3D all-metal aromatic Al_6^{2-} cluster. The aromaticity is still maintained! However, fusion of two 2D all-metal aromatic Al_4^{2-} units results in the larger Al_8-cluster, where the aromaticity is destroyed.

Although no examples have been identified experimentally as yet, the novel sandwich-like compounds $[CpMAl_4]^{q-}$, $(Li)_q[CpMAl_4]$ $[CpMAl_4MCp]^{q-}$ are unusual in that they combine an organic aromatic unit Cp^- and an exotic all-metal aromatic unit Al_4^{2-}. They extend our knowledge of sandwich-type complexes and promise to enrich and to bridge organic and inorganic chemistry. The unusual structures of our designed hetero-decked sandwich-like compounds may confer special properties that may be usefully employed in the design of new materials. Our computational results challenge preparative chemists (e.g. photoelectron spectroscopy studies or deck-exchange reactions in solution). Moreover, our designed main-group metal sandwich compounds are charge-transfer species and might thus become ideal candidates for designing molecular materials with large NLO coefficients.

Our extensive study has important implications in various fields. Firstly, the hetero-decked sandwich scheme should also apply to higher alkali metals (Rb, Cs) and alkaline-earth metals (Sr, Ba) as well as to other experimentally known all-metal aromatic units D^{q-}, such as XAl_3^- (X = Si, Ge, Sn, Pb), M_4^{2-} (M = Ga, In, Tl), M_3^- (M = Al, Ga), when utilising them in assembled molecular compounds. Yet, the homo-decked sandwich scheme, which is typical for metallocenes CpMCp, cannot lead to stable DMD (D = all-metal aromatic deck) species for synthesis. The present results should open a new route to the design of assembled molecular compounds based on the all-metal aromatic species. Secondly, compared to the traditional metallocenes with all-Cp^- decks that have organic aromaticity,

Table 3. The aromaticity (NICS(0) and NICS(1)) of the Al_4 rings in all of the sandwich forms (f–f and f–s) of $[CpMAl_4]^{q-}$ (q = 2, M = Li, Na, K; q = 1, M = Be, Mg, Ca) and the aromaticity of comparative Al_4^{2-} were calculated at B3LYP/6-311 + G(d) level.

M	$[CpMAl_4]^{q-}$	Face–face (f–f)		Face–side (f–s)	
		NICS(0)	NICS(1)	NICS(0)	NICS(1)
Li	$^1[CpLiAl_4]^{2-}$	−32.18	−25.19	−36.56	−28.69
Na	$^1[CpNaAl_4]^{2-}$	−30.66	−24.83	−36.58	−28.69
K	$^1[CpKAl_4]^{2-}$	−30.61	−25.29	−35.19	−27.77
Be	$^1[CpBeAl_4]^-$	−31.24	−21.82	−38.27	−29.53
Mg	$^1[CpMgAl_4]^-$	−22.35	−18.94	−38.30	−29.70
Ca	$^1[CpCaAl_4]^-$	−24.16	−21.09	−34.05	−26.71
	Al_4^{2-}	NICS(0) = −34.46		NICS(1) = −27.39	

our designed $[CpMAl_4]^{q-}$ represents a new class of metallocenes containing the all-metal aromatic Al_4^{2-} units. Thirdly, during the hetero-decked sandwiching process, the multiple aromaticity and characteristic orbitals of Al_4^{2-} are well kept. Thus, the Al_4^{2-} unit could indeed act as a "superatom",[18] when assisted by a rigid partner such as Cp^-. To the best of our knowledge, this is the first theoretical evidence to support the hypothesis that the all-metal aromatic Al_4^{2-} is a new example of a "superatom". Future studies on the "superatom" chemistry of Al_4^{2-} are greatly desired. Finally, based on the above four points, the newly proposed concept "hetero-decked sandwich" bridges the all-metal aromaticity, metallocenes and "superatom" chemistry and is thus well-suited to combinational chemistry. Based on this concept, various interesting species could be designed.

Conclusion

In summary, we performed very detailed DFT studies on six systems $[DAl_4M]^{q-}$ ($D = Al_4^{2-}$, Cp^-; M = Li, Na, K, Be, Mg, Ca), that contained model compounds and saturated compounds for both homo-decked and hetero-decked schemes. We found seven new homo-decked sandwich forms $[Al_4MAl_4]^{q-}$ (M = Li, Na, K, Be, Mg, Ca) to be energy minima and possess the all-metal aromatic unit Al_4^{2-}. Unfortunately, our detailed structure search showed that all seven homo-decked sandwich forms $[Al_4MAl_4]^{q-}$ are high-lying and eventually transform into the lower-lying fused Al_8 clusters under thermal conditions. Instead, we proposed and applied a new scheme for stabilising the Al_4^{2-} unit in sandwich forms, namely as Al_4^{2-} and the well-known organic aromatic unit Cp^- that can cooperatively sandwich alkali metal and alkaline-earth metal atoms. Various extended compounds have been designed. When assisted by a rigid unit, such as Cp^-, the all-metal aromatic unit Al_4^{2-} can indeed be used as a novel "superatom". The new concept "hetero-decked sandwich" may lead to boundless possibilities for the design of novel molecular species associated with all-metal aromaticity, metallocenes, superatoms and combinational chemistry. The first type of synthesisable sandwich complexes $(Li)_q[CpMAl_4]$ with the all-metal aromatic unit Al_4^{2-} awaits future experimental verification. The present results are expected to provide an insight for future molecular designs based on other all-metal aromatic units.

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[1] a) X. Li, A. E. Kuznetsov, H. F. Zhang, A. I. Boldyrev, L. S. Wang, *Science* **2001**, *291*, 859–861; b) S. K. Ritter, *Chem. Eng. News* **2001**, *79* (39), 39–40; c) D. K. Seo, J. D. Corbett, *Science* **2001**, *291*, 841–842.

[2] X. Li, H. F. Zhang, L. S. Wang, A. E. Kuznetsov, N. A. Cannon, A. I. Boldyrev, *Angew. Chem.* **2001**, *113*, 1919–1922; *Angew. Chem. Int. Ed.* **2001**, *40*, 1867–1870.

[3] a) A. E. Kuznetsov, A. I. Boldyrev, X. Li, L. S. Wang, *J. Am. Chem. Soc.* **2001**, *123*, 8825–8831; b) B. Twamley, P. P. Power, *Angew. Chem.* **2000**, *112*, 3643–3646; *Angew. Chem. Int. Ed.* **2000**, *39*, 3500–3503.

[4] a) A. Cisar, J. D. Corbett, *Inorg. Chem.* **1977**, *16*, 2482–2487; b) S. C. Critchlow, J. D. Corbett, *Inorg. Chem.* **1984**, *23*, 770–774; c) K. Tanaka, T. Yamabe, H. Teramae, K. Fukui, *Inorg. Chem.* **1979**, *18*, 3591–3595; d) J. Kao, *J. Mol. Struct.* **1980**, *63*, 293–298; e) T.-H. Tang, R. F. W. Bader, P. J. MacDougall, *Inorg. Chem.* **1985**, *24*, 2047–2052; f) F. L. Skrezenek, R. D. Harcourt, *Theor. Chim. Acta.* **1985**, *67*, 271–276; g) L. J. Saethre, O. Gropen, *Can. J. Chem.* **1992**, *70*, 348–353; h) M. Sannigrahi, F. Grein, *Can. J. Chem.* **1994**, *72*, 298–302; i) I. Krossing, J. Passmore, *Inorg. Chem.* **1999**, *38*, 5203–5206; j) H. D. B. Jenkins, L. C. Jitariu, I. Krossing, J. Passmore, R. Suontamo, *J. Comput. Chem.* **2000**, *21*, 218–223; k) H. M. Tuononen, R. Suontamo, J. Valkonen, R. S. Laitinen, *J. Phys. Chem. A* **2004**, *108*, 5670–5676.

[5] a) R. J. Gillespie, J. Barr, R. Kapoor, K. C. Malhotra, *Can. J. Chem.* **1968**, *46*, 149–153; b) R. J. Gillespie, J. Barr, D. B. Crump, R. Kapoor, P. K. Ummat, *Can. J. Chem.* **1968**, *46*, 3607–3612; c) J. Barr, R. J. Gillespie, R. Kapoor, G. P. Pez, *J. Am. Chem. Soc.* **1968**, *90*, 6855–6860; d) T. W. Couch, D. A. Lokken, J. D. Corbett, *Inorg. Chem.* **1972**, *11*, 357–362; e) N. Burford, J. Passmore, J. C. P. Sanders, *From Atoms to Polymers. Isoelectronic Analogies* (Eds.: J. F. Liebman, A. Greenburg), VCH, New York, **1989**, pp. 53–108.

[6] a) X. Li, X. B. Wang, L. S. Wang, *Phys. Rev. Lett.* **1998**, *81*, 1909–1912; b) H. Wu, X. Li, X. B. Wang, C.-F. Ding, L. S. Wang, *J. Chem. Phys.* **1998**, *109*, 449–458; c) K. K. Baeck, R. J. Bartlett, *J. Chem. Phys.* **1998**, *109*, 1334–1342; d) A. E. Kuznetsov, A. I. Boldyrev, *Struct. Chem.* **2002**, *12*, 141–148; e) C.-G. Zhan, F. Zheng, D. A. Dixon, *J. Am. Chem. Soc.* **2002**, *124*, 14795–14803; f) A. E. Kuznetsov, A. I. Boldyrev, H.-J. Zhai, X. Li, L.-S. Wang, *J. Am. Chem. Soc.* **2002**, *124*, 11791–11801.

[7] a) J. W. Nielsen, N. C. Baenziger, *Acta Crystallogr.* **1954**, *10*, 277–284; b) J. D. Corbett, *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 81–86; c) A. E. Kuznetsov, J. D. Corbett, L. S. Wang, A. I. Boldyrev, *Angew. Chem.* **2001**, *113*, 3473–3476; *Angew. Chem. Int. Ed.* **2001**, *40*, 3369–3372.

[8] a) I. Todorov, S. C. Sevov, *Inorg. Chem.* **2004**, *43*, 6490–6494; b) I. Todorov, S. C. Sevov, *Inorg. Chem.* **2005**, *44*, 5361–5369.

[9] a) M. Gausa, R. Kaschner, H. O. Lutz, G. Seifert, K.-H. Meiwes-Broer, *Chem. Phys. Lett.* **1994**, *230*, 99–103; b) M. Gausa, R. Kaschner, G. Seifert, J.-H. Faehrmann, H. O. Lutz, K.-H. Meiwes-Broer, *J. Chem. Phys.* **1996**, *104*, 9719–9724; c) H. J. Zhai, L. S. Wang, A. E. Kuznetsov, A. I. Boldyrev, *J. Phys. Chem. A* **2002**, *106*, 5600–5606.

[10] a) H. Tanaka, S. Neukermans, E. Janssens, R. E. Silverans, P. Lievens, *J. Am. Chem. Soc.* **2003**, *125*, 2862–2863; b) A. N. Alexandrova, A. I. Boldyrev, H.-J. Zhai, L. S. Wang, *J. Phys. Chem. A* **2005**, *109*, 562–570; c) C. S. Wannere, C. Corminboeuf, Z.-X. Wang, M. D. Wodrich, R. B. King, P. von R. Schleyer, *J. Am. Chem. Soc.* **2005**, *127*, 5701–5705.

[11] M. Lein, J. Frunzke, G. Frenking, *Angew. Chem.* **2003**, *115*, 1341–1345; *Angew. Chem. Int. Ed.* **2003**, *42*, 1303–1306.

[12] a) A. I. Boldyrev, L. S. Wang, *Chem. Rev.* **2005**, *105*, 3716–3757, and references therein. b) C. A. Tsipis, *Coord. Chem. Rev.* **2005**, *249*, 2740–2762, and references therein.

[13] a) A. E. Kuznetsov, A. I. Boldyrev, X. Li, L. S. Wang, *J. Am. Chem. Soc.* **2001**, *123*, 8825–8831; b) A. E. Kuznetsov, J. D. Corbett, L. S. Wang, A. I. Boldyrev, *Angew. Chem.* **2001**, *113*, 3473–3476; *Angew. Chem. Int. Ed*, **2001**, *40*, 3369–3372; c) C.-G. Zhan, F. Zheng, D. A. Dixon, *J. Am. Chem. Soc.* **2002**, *124*, 14795–14803; d) P. W. Fowler, R. W. A. Havenith, E. Steiner, *Chem. Phys. Lett.* **2002**, *359*, 530–536; e) R. W. A. Havenith, J. H. v. Lenthe, *Chem. Phys. Lett.* **2004**, *385*, 198–201.

[14] a) J. M. Mercero, J. M. Ugalde, *J. Am. Chem. Soc.* **2004**, *126*, 3380–3381; b) J. M. Mercero, E. Formoso, J. M. Matxain, L. A. Eriksson, J. M. Ugalde, *Chem. Eur. J.* **2006**, *12*, 4495–4502; c) E. Urnezius, W. W. Brennessel, C. J. Cramer, J. E. Ellis, P. von R. Schleyer, *Science* **2002**, *295*, 832–834; d) M. Lein, J. Frunzke, G. Frenking, *Inorg. Chem.* **2003**, *42*, 2504–2511; e) J. Frunzke, M. Lein, G. Frenking, *Organometallics* **2002**, *21*, 3351–3359; f) J. M. Mercero, J. M. Matxain, J. M. Ugalde, *Angew. Chem.* **2004**, *116*, 5601–5604; *Angew. Chem. Int. Ed.* **2004**, *43*, 5485–5488; g) L. P. Cheng, Q. S. Li, *J. Phys. Chem. A* **2003**, *107*, 2882–2889; h) L. P. Cheng, Q. S. Li, *J. Phys. Chem. A* **2005**, *109*, 3182–3186; i) J. Guan, Q. S. Li, *J. Phys. Chem. A* **2005**, *109*, 9875–9881.

[15] For example, see: R. E. Dinnebier, U. Behrens, F. Olbrich, *Organometallics* **1997**, *16*, 3855–3858.

[16] a) A. Datta, S. K. Pati, *J. Am. Chem. Soc.* **2005**, *127*, 3496–3500; b) A. Datta, S. K. Pati, *Chem. Commun.* **2005**, 5032–5034; c) A. Datta, S. K. Pati, *J. Phys. Chem. A* **2004**, *108*, 9527–9530.

[17] a) T. J. Peckham, P, Gomez-Elipe, I. Manners, *Metallocenes, Vol. 2* (Eds.: A. Togni, R. L. Halterman), Wiley-VCH, Weinheim, **1998**, p. 724; b) I. Resa, E. Carmona, E. Gutierrez-Puebla, A. Monge, *Science* **2004**, *305*, 1136–1138; c) G. Parkin, *Science* **2004**, *305*, 1117–1118.

[18] a) D. E. Bergeron, A. W. Castleman, Jr., T. Morisato, S. N. Khanna, *Science* **2004**, *304*, 84–87; b) D. E. Bergeron, P. J. Roach, A. W. Castleman, N. Jones, S. N. Khanna, *Science* **2005**, *307*, 231–235.

[19] a) A. D. McLean, G. S. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639–5648; b) T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. von R. Schleyer, *J. Comput. Chem.* **1983**, *4*, 294–299; c) M. J. Frisch, J. A. Pople, J. S. Binkley, *J. Chem. Phys.* **1984**, *80*, 3265–3269.

[20] a) R. G. Parr, W. Yang, *Density-functional theory of atoms and molecules*; Oxford University Press: Oxford, **1989**; b) A. D. Becke, *J. Chem. Phys.* **1992**, *96*, 2155–2160; c) J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais, *Phys. Rev. B* **1992**, *46*, 6671–6687.

[21] All calculations were performed with the Gaussian 03 program package. Gaussian 03 (Revision A.1), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda,O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **2003**.

[22] V. I. Minkin, M. N. Glukovtsev, B. Y. Simkin, *Aromaticity and Antiaormaticity*, Wiley, New York, **1994**.

[23] Z. Chen, C. S. Wannere, C. Corminbeouf, R. Puchta, P. von R. Schleyer, *Chem. Rev.* **2005**, *105*, 3842–3888.

[24] a) Z. Chen, C. Corminbeouf, T. Heine, J. Bohmann, P. von R. Schleyer, *J. Am. Chem. Soc.* **2003**, *125*, 13930–13931; b) Y. Jung, T. Heine, P. von R. Schleyer, M. Head-Gordon, *J. Am. Chem. Soc.* **2004**, *126*, 3132–3138.

[25] a) A. C. Tsipis, C. A. Tsipis, *J. Am. Chem. Soc.* **2003**, *125*, 1136–1137; b) C. A. Tsipis, E. E. Karagiannis, P. F. Kladou, A. C. Tsipis, *J. Am. Chem. Soc.* **2004**, *126*, 12916–12929; c) X. Huang, H. J. Zhai, B. Kiran, L. S. Wang, *Angew. Chem.* **2005**, *117*, 7417–7420; *Angew. Chem. Int. Ed.* **2005**, *44*, 7251–7254; d) C. S. Corminboeuf, C. S. Wannere, D. Roy, R. B. King, P. von R. Schleyer, *Inorg. Chem.* **2006**, *45*, 214–219.

[26] L. M. Yang, Y. H. Ding, C. C. Sun, Unpublished results.

[27] a) All MO pictures were created with the MOLDEN 3.4 program. b) G. Schaftenaar, MOLDEN 3.4, CAOS/CAMM Center, The Netherlands, **1998**.

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