New examples of metalloaromatic Al-clusters: $(Al_4M_4)Fe(CO)_3$ ($M = Li$, Na and K) and $(Al_4M_4)_2Ni$: rationalization for possible synthesis†

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***Ab initio* calculations reveal that all-metal antiaromatic molecules like Al_4M_4 ($M = Li$, Na and K) can be stabilized in half sandwich $(Al_4M_4)Fe(CO)_3$ and full sandwich $(Al_4M_4)_2Ni$ complexes. The formation of the full sandwich complex $[(Al_4M_4)_2Ni]$ from its organometallic precursor depends on the stability of the organic–inorganic hybrid $(C_4H_4)Ni(Al_4Li_4)$.**

The concept of aromaticity and antiaromaticity is of fundamental importance to structural chemistry.[1–3] This concept has been recently extended from organic molecules to metallic systems like those of Al and Sn.[4,5] Molecules like Li_4Al_4, Na_4Al_4 and their anions ($Li_3Al_4^-$ and $Na_3Al_4^-$) have been recently shown as the first examples of antiaromatic metal clusters due to their close resemblance to C_4H_4, from both structural and electronic points of view.[6] Also, very recently, we have shown that these clusters can be highly stabilized by complexation with 3d metal atoms like Fe and Ni, which results in metalloaromaticity in these Al_4 clusters, with an increase in the number of π electrons from 4π to 6π.[7] This is very similar in concept to the onset of aromaticity in C_4H_4 on complexation originally proposed by Longuet-Higgins and Orgel,[8a] and synthesized soon after by Criegee and Schroder.[8b] The counterions in Al_4M_4 ($M = Li$, Na and K), being highly electropositive, lose their electrons to the Al_4 ring, thereby making it formally -4-charged and thus a 4π antiaromatic system. Al_4M_4 can thus be considered as isolobal with C_4H_4 and is expected to follow similar reactivity patterns to C_4H_4.[9] The role of the counterions have, however, not been investigated until now. In this work we critically examine their role and propose methodologies for their possible experimental synthesis through step-wise formation of half sandwich all-metal complexes, hybrid organo–inorganic complexes, and finally, full sandwich all-metal complexes. We also study the bonding aspects in the first mixed sandwich (hybrid) complexes of type $(Al_4M_4)(C_4H_4)Ni$. Interestingly, we find that these hybrid sandwich complexes have admixtured interactions with the transition metal atoms and organic/inorganic ligands, and can be considered as candidates for future synthesis.

The structures considered in the present work: $(Al_4M_4)Fe(CO)_3$, sandwich complexes of the type $(Al_4M_4)_2Ni$ and the hybrid sandwich complexes $(Al_4M_4)Ni(C_4H_4)$, with $M = Li$, Na and K, were optimized based on the B3LYP/6-31G(d,p)+ method[10] (see ESI for details†). Fragmentation energy analysis and calculations of the HOMO–LUMO gaps were performed at the B3LYP/6-311G(d,p)++ level. The same level of calculations were also performed for the uncoordinated Al_4M_4 and C_4H_4. We first discuss the structural features in the uncoordinated ligands Al_4M_4. There are some remarkable similarities in their structures with variation of the alkali metal ion. The ground state minimum energy form for all the ligands possesses a C_{2h} symmetry (see Fig. 1).

Another very important feature to be noted for these molecules is that the ground state geometry for all the ligands has a substantial bond length alteration (BLA) (0.124 Å for Al_4Li_4, 0.11 Å for Al_4Na_4 and 0.10 Å for Al_4K_4). BLA is defined as the bond length difference between two consecutive Al–Al bonds in the central four-membered Al_4 ring. For their organic analogue C_4H_4, the BLA is 0.245 Å. While the magnitude of the BLA in these clusters is smaller than that for the π-conjugated antiaromatic molecule C_4H_4, it is more than that found in aromatic molecules like benzene ($BLA = 0$ for benzene), and thus these clusters are both σ-aromatic as well as π-antiaromatic.[6a,11] We have calculated the nucleus-independent chemical shift (NICS) at the GIAO-B3LYP/6-311G(d,p)++ level for these molecules.[12] The NICS values for Al_4Li_4, Al_4Na_4 and Al_4K_4 are -11.55, -7.91 and -7.72 ppm, respectively. Interestingly, with the variation in size of the alkali metal, we find that the extent of NICS aromaticity decreases with increasing size of counterion. This is understood from the fact that the ionization potentials of M decrease in the order $Li > Na > K$. Thus, the extent of charge transfer is maximum from the K ions to the Al_4 ring in Al_4K_4 and is strongly π-antiaromatic, which reduces the magnitude of the σ-aromaticity. A similar conclusion is also derived from the magnitudes of the HOMO–LUMO gaps. The gaps for Al_4Li_4, Al_4Na_4 and Al_4K_4 are 1.45, 1.25 and 0.74 eV, respectively. The much smaller gap for Al_4K_4 signifies high reactivity, smaller chemical hardness and poor overall aromatic character.[13]

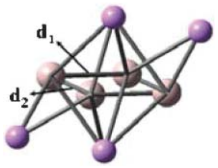

Fig. 1 Ground state geometry for Al_4M_4. Bond distances d_1 and d_2 (in Å) are 2.68 and 2.56 for Al_4Li_4, 2.70 and 2.59 for Al_4Na_4, and 2.67 and 2.58 for Al_4K_4, respectively. See ESI for coordinates and energies of these geometries.†

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† Electronic Supplementary Information (ESI) available: Ground state optimized geometries, cartesian coordinates, total energies in Hartrees and frontier orbital plots. See http://dx.doi.org/10.1039/b508123h

In the complex $(Al_4M_4)Fe(CO)_3$, in all the cases with variation of M, the ligand binds strongly with the Fe atom, forming an η^4 coordination. A very remarkable feature in these complexes is that in the Al_4^{4-} rings, the BLA is very small [0.028, 0.0345 and 0.041 Å in $(Al_4Li_4)Fe(CO)_3$, $(Al_4Na_4)Fe(CO)_3$ and $(Al_4K_4)Fe(CO)_3$, respectively].

This suggests that the ligand interacts with the d-orbitals of the Fe atom, with a transfer of 2 electrons from the metal to the ligand (metal to ligand charge transfer, MLCT), making the Al_4 ring an effective 6π electron aromatic system. Also note that, for M = K, the BLA is the maximum in the series, consistent with the smallest net aromaticity, as supported by NICS and HOMO–LUMO gap calculations. The net stability of the complexes are measured using the fragmentation scheme: $(Al_4M_4)Fe(CO)_3 = Al_4M_4 + Fe(CO)_3$; where the constituents are in their stable ground state geometric configurations. The binding energy (defined as $E_{\text{complex}} - E_{\text{fragments}}$) in $(Al_4Li_4)Fe(CO)_3$, $(Al_4Na_4)Fe(CO)_3$ and $(Al_4K_4)Fe(CO)_3$ are −118.85, −122.92 and −126.28 kcal mol^{-1}, respectively. For comparison, we have also calculated the binding energy in $(C_4H_4)Fe(CO)_3$, which is −70 kcal mol^{-1}. The substitution reactions are shown in Fig. 2.

The large stability associated with these molecules is due to the formation of a stable, closed shell, 18 electron configuration in each case.[14]

The binding energy for $(Al_4K_4)Fe(CO)_3$ is the highest, suggesting that in such complexes, only the π electrons on the ring interact with the metal 3d orbitals, the poor σ–π separation initially existing in the ligand is lifted, and the system behaves as an 18 electron stable molecule. This is a very important result as one can fine tune the σ–π separations by functionalizing the Al_4^{4-} rings with appropriate electropositive counterions. The magnitudes of the HOMO–LUMO gaps for the $(Al_4Li_4)Fe(CO)_3$, $(Al_4Na_4)Fe(CO)_3$ and $(Al_4K_4)Fe(CO)_3$ complexes decrease in the order 3.34, 2.31 and 1.85 eV, respectively, suggesting the softer nature of the Al_4K_4 ligand. Another major change that is associated with the formation of the complexes is that the structure of the counterions are lost completely on complexation. As already mentioned, the counterions are arranged around the Al_4 ring so as to result in a C_{2h} symmetry. However, on complexation with the transition metal atoms, the symmetry is completely lost. There is an overall loss in energy in the order of 20 kcal mol^{-1}, compared to the ground state structure of Al_4M_4, but the stability associated with the formation of the complex with the 3d metal atom overwhelms the structural instability in the ligand.

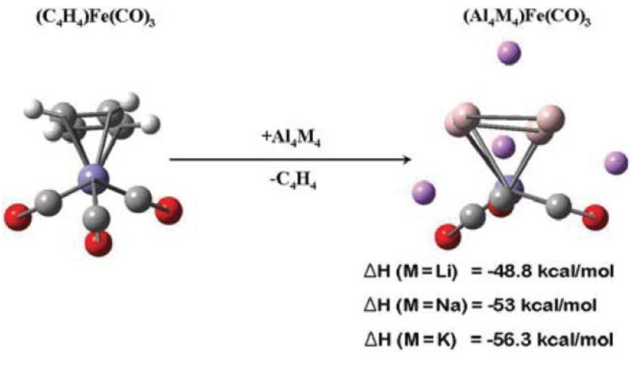
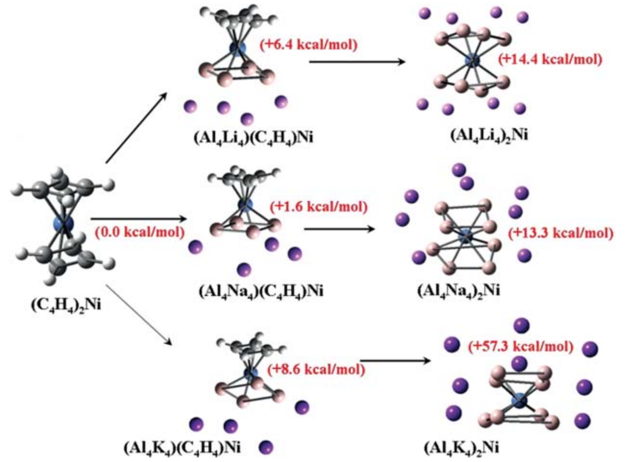


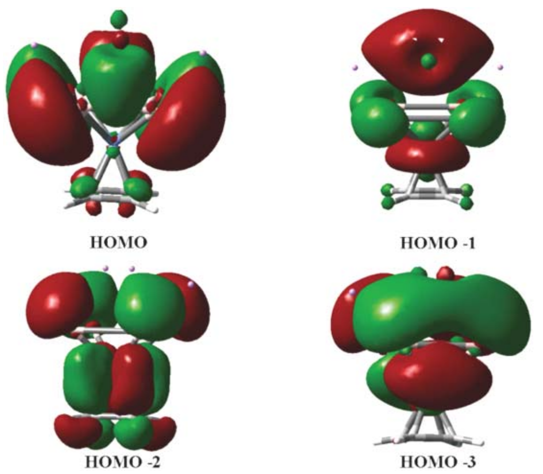
Fig. 2 Substitution reactions in $(C_4H_4)Fe(CO)_3$ by Al_4Li_4, Al_4Na_4 and Al_4K_4 to produce $(Al_4Li_4)Fe(CO)_3$, $(Al_4Na_4)Fe(CO)_3$ and $(Al_4K_4)Fe(CO)_3$, respectively. Note that all these substitutions are highly exothermic. Small filled pink circles indicate the alkali metal ions.



Scheme 1 Step-wise synthesis for all-metal sandwich complexes from organometallic complex $(C_4H_4)_2Ni$. The energy for $(C_4H_4)_2Ni$ has been scaled to zero to show the endothermic substitution reactions. Small filled pink circles indicate the alkali metal ions.

Another very well known route for stabilizing these unstable ligands is through the formation of sandwich complexes similar to ferrocene.[15] For 4π electronic systems like C_4H_4, $(C_4H_4)_2Ni$ is a well stabilized complex.[16] Similarly, we have stabilized sandwich complexes of the type $(Al_4M_4)_2Ni$, having binding energies similar to those of their organic analogues. The binding energies for $(Al_4Li_4)_2Ni$, $(Al_4Na_4)_2Ni$ and $(Al_4K_4)_2Ni$ are −146.05, −147.12 and −103.12 kcal mol^{-1}, respectively. Note that lower stabilization in $(Al_4K_4)_2Ni$ arises from the distortion of the sandwich architecture due to the presence of bulky K^+ ions (see structure in Scheme 1), as a result of which the average K^+ ion distance to the Al_4^{4-} ring is very large (3.5 Å). For $(Al_4Li_4)_2Ni$ and $(Al_4Na_4)_2Ni$, the average M^+ distance from the Al_4^{4-} ring is 3.0 Å. This is also evident from the decreasing order of the HOMO–LUMO gaps for these complexes (1.623, 1.323 and 0.954 eV for $(Al_4Li_4)_2Ni$, $(Al_4Na_4)_2Ni$ and $(Al_4K_4)_2Ni$, respectively). On the other hand, the binding energy for $(C_4H_4)_2Ni$ is calculated to be −160.42 kcal mol^{-1}, and thus, unlike the cases for $(Al_4M_4)Fe(CO)_3$, direct substitution of C_4H_4 with Al_4M_4 will be highly endothermic, making it quite unfavourable. For a detailed understanding of the highly exothermic formation of $(Al_4M_4)Fe(CO)_3$ compared to the endothermic substitution product $(Al_4M_4)_2Ni$, the HOMO orbitals for both systems have been analysed.† The HOMO for $(Al_4M_4)Fe(CO)_3$ shows substantially more intermixing between the d-orbitals of the $Fe(CO)_3$ fragment and the π orbitals of Al_4M_4, leading to stronger complexation in the case of $(Al_4M_4)Fe(CO)_3$. The presence of three strong π-acceptor CO ligands in the $Fe(CO)_3$ fragment leads to quenching of the d-orbitals on the Fe atom and thereby facilitates stronger binding between the Al_4M_4 ligand and the $Fe(CO)_3$ fragment.

In view of the above, we follow here a different strategy. We consider a substitution reaction of the type: $(C_4H_4)_2Ni + Al_4M_4 \rightarrow (C_4H_4)Ni\,(Al_4M_4) + C_4H_4$. As already mentioned, the Al_4M_4 binds more strongly to the metal center than does C_4H_4. Therefore, we expect that it is possible to synthesise a hybrid organic–inorganic sandwich complex. These hybrid complexes are very interesting


HOMO

HOMO -1

HOMO -2

HOMO -3

Fig. 3 Frontier orbital diagrams in mixed sandwich complex $(Al_4Li_4)Ni(C_4H_4)$.

because, while for the C_4H_4 ligand the interaction with the transition metal atom involves only the π electrons, for the Al_4M_4 ligand the interactions are through both the σ and π orbitals. Interestingly, the extent of involvement of the σ and π orbitals in the interaction also depends on the nature of the counterions present. In Fig. 3, we show the frontier orbital plots for $(C_4H_4)Ni(Al_4Li_4)$. Similar features are also seen in the cases of $(C_4H_4)Ni(Al_4Na_4)$ and $(C_4H_4)Ni(Al_4K_4)$. From these orbitals it is clear that the ligand group orbitals (LGOs) on Al_4M_4 interact much more strongly with the transition metal (Ni) orbitals. Specifically, the d_z^2, d_{xz} and d_{xy} orbitals of Ni interact with the LGOs of Al_4M_4 in HOMO-1, HOMO-2 and HOMO-3, respectively. On the contrary, the LGOs of C_4H_4 interact very weakly with the transition metal orbitals, as a result of which, the binding of the organic ligand with the transition metal is much weaker compared to that for Al_4M_4 in these mixed sandwich complexes. The structures of these hybrid complexes are found to be quite stable. The heat of formation of $(C_4H_4)Ni(Al_4Li_4)$, $(C_4H_4)Ni(Al_4Na_4)$ and $(C_4H_4)Ni(Al_4K_4)$ are -153.93, -158.82 and -151.80 kcal mol^{-1}, respectively. This is in marked contrast to that for the previous complexes, where the heat of formation of the complexes increased monotonically with the increase in the size of the counterion (Fig. 3). The HOMO–LUMO gaps in the hybrid complexes, however, follow the same trend as for other complexes: 2.01 eV [$(C_4H_4)Ni(Al_4Li_4)$], 1.96 eV [$(C_4H_4)Ni(Al_4Na_4)$] and 1.35 eV [$(C_4H_4)Ni(Al_4K_4)$]. The BLA for C_4H_4 and Al_4M_4 are 0.0092 and 0.0386Å in $(C_4H_4)Ni(Al_4Li_4)$, 0.0106 and 0.0168 Å in $(C_4H_4)Ni(Al_4Na_4)$, and 0.0033 and 0.10459 Å in $(C_4H_4)Ni(Al_4K_4)$, respectively. Note that for M = K, the Al_4K_4 unit has a substantial BLA, with a magnitude close to that of uncoordinated Al_4K_4. This explains the smaller binding energy of the hybrid complex with the K^+ counterions, as compared to $(C_4H_4)Ni(Al_4Li_4)$ and $(C_4H_4)Ni(Al_4Na_4)$. However, compared to the $Fe(CO)_3$ complexes, these complexes are softer as the HOMO–LUMO gap is quite small.

We would like to rationalize the synthesis of these sandwich complexes in a 3-step reaction of the type: $(C_4H_4)Ni(C_4H_4) \rightarrow (C_4H_4)Ni\ (Al_4M_4)$, and finally, $\rightarrow (Al_4M_4)Ni\ (Al_4M_4)$ (shown in Scheme 1).

As already shown, the hybrid intermediates $(C_4H_4)Ni(Al_4M_4)$ are quite stable and can thus be isolated. However, these substitution reactions are mildly endothermic (contrary to those for the $Fe(CO)_3$ complexes). In this series, the heat of formation is least endothermic for both $(Al_4Na_4)Ni(C_4H_4)$ and $(Al_4Na_4)_2Ni$, and so these are the best candidates for isolation.

To conclude, we propose experimental methodologies for the possible synthesis of the first examples of all-metal half sandwich, mixed sandwich and full sandwich complexes. Based on our high level density functional theory calculations, we have shown that while half sandwich complexes can be readily formed due to the presence of π-accepting ligands like CO, the formation of mixed and full sandwich complexes is endothermic.

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