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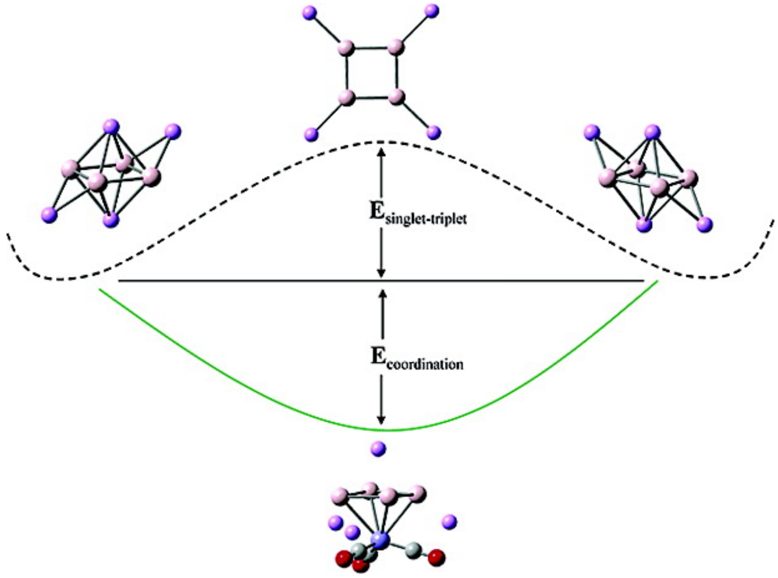

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Stable Transition Metal Complexes of an All-Metal Antiaromatic Molecule (Al_4Li_4): Role of Complexations

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Abstract: We propose for the first time a few examples of stable transition metal complexes of an all-metal antiaromatic molecule Al_4Li_4. We demonstrate that these all-metal species can be stabilized by complexation with 3d transition metals very similar to their organic counterpart, C_4H_4. Complexation to transition metal ions reduces the frontier orbital energies and introduces aromatic charactersitics. We consider a series of such complexes: [η^4-(Al_4Li_4)-$Fe(CO)_3$, η^2,σ^2-(Al_4Li_4)-Ni, and $(Al_4Li_4)_2Ni$] and compare and contrast their energetics with their organometallic counterparts. Fragmentation energy, orbital correlation energy analysis, and the nucleus-independent chemical shift (NICS) values support the complexation-induced stabilities in these systems.

The concept of aromaticity and antiaromaticity is of fundamental importance in chemistry. From the simple Hückel theory to more refined concepts such as ring currents and critical point charge densities, the field has evolved over a period of a half century.[1] The idea has been extended from initially a small class of organic π-conjugated systems to now many inorganic molecules and molecular clusters,[2] with rapid experimental verifications through actual synthesis and characterizations.[3]

In the past few years there have been reports of aromaticity in all-metal clusters.[4] The recent report of the first all-metal antiaromatic complex, Al_4Li_4, shows the generalizations and usefulness of the concept.[5] However, unlike their organic counterpart, C_4H_4, where the energy separation between the σ and π orbitals is substantial, these all-metal molecules have closely placed orbitals and thus have poor $\sigma-\pi$ separation. Mostly, the aromatic characteristic is associated with delocalized electrons (π electrons). However, recently it has been reported that these clusters are more σ aromatic than π antiaromatic.[5,6] As a result, there has been confusion whether to call these complexes aromatic or antiaromatic.[7] The controversy can only be settled after the successful synthesis followed by unambiguous crystal structure determinations. For a stable molecular crystal, measurement of bond length alternations as well as the charge densities (ring critical points) are well-established parameters for characterizing aromaticity/antiaromaticity.[8]

These clusters, however, have until now been synthesized only in the gas phase by the laser vaporization technique, which is thus insufficient in providing structural details. Recently, we have shown that these materials, Al_4M_4 (M = Li, Na, and K) are also very good candidates for higher order nonlinear optical (NLO) applications due to charge transfer from the highly electropositive ion (Li) to the Al_4 rings.[9] Unfortunately, stability is one issue that hinders any applications let alone firm establishment of a basic understanding.

The synthesis of antiaromatic molecules is difficult because of their instabilities. Cyclobutadiene (C_4H_4), a 4π-electron system, remained nonisolated for a long time before Longuet-Higgins and Orgel proposed, in a landmark paper, the concept of stabilization through complexation with a transition metal to form an organometallic compound.[10] The compound was synthesized soon after.[11] In the following, we justify this simplistic model for the small Al_4 clusters and propose a few very stable complexes of these all-metal species. At the same time, we also compare and contrast the energetics with their organic analogues (C_4H_4 complexes).

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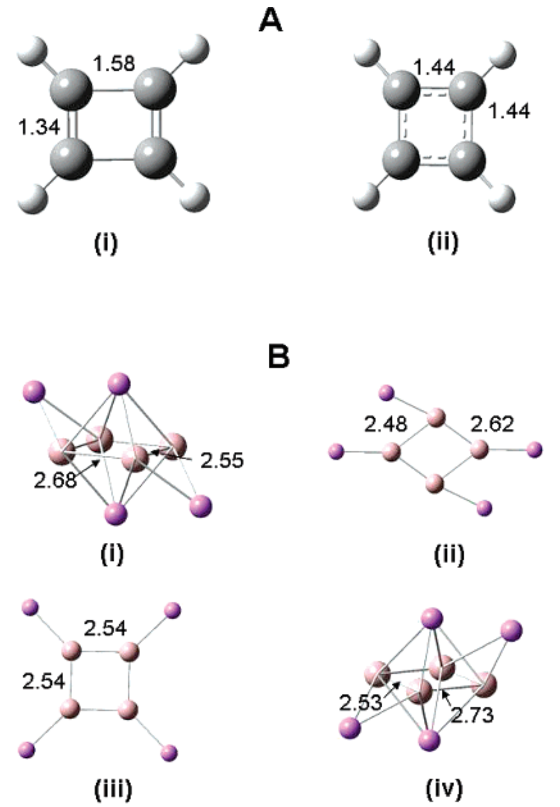

Figure 1. Equilibrium minimum energy geometries for C_4H_4 and Al_4Li_4 in singlet and triplet states. (See Table 1.) Bond lengths are given in Å. Ball color: black = C, white = H, pink = Li, light orange = Al.

We have performed a closed-shell calculation for the singlet state and an open-shell calculation for the triplet state at the 6-311G(d,p) basis set level. Electron correlation has been included according to density functional theory using Becke's three-parameter hybrid formalism and the Lee−Yang−Parr functionals (B3LYP) available in the Gaussian electronic structure set of codes.[12] The geometries obtained from the B3LYP method have been shown to be in very good agreement with the measured photoelectron spectra in such small clusters.[13]

In Figure 1, the minimum energy ground-state structures are shown for C_4H_4 and Al_4Li_4. Simple Hückel π-electron theory predicts a triplet square geometry for C_4H_4 with equal C−C bond lengths.[14] However, inclusion of interaction with the underlying σ backbone stabilizes the C_4H_4 molecule in a singlet state with rectangular geometry. This is a good example of Jahn−Teller distortion or Pierls instability in a low-dimensional system that allows stabilizations through bond length alternation. In fact, in this picture, the square geometry actually corresponds to a transition state between two degenerate rectangular ground-state structures. In Table 1, the total energies and bond length alternation (Δr, defined as the average difference between the bond lengths of two consecutive bonds in the four-membered ring) for both states are tabulated. The rectangular C_4H_4 [Figure 1A(i)] is more stable than the square geometry [Figure 1A(ii)] by 6.2 kcal/mol. Thus, a triplet square geometry is expected to be the transition state for processes such as ring whizzing, where one rectangular form is converted into the other (an in-plane rotation of 90°), in harmony with time-resolved transition-state studies for the tub inversion in 1,3,5,7-cyclooctatetraene.[15]

Table 1. Total Energies (in au) and Bond Length Alternation, Δr (in Å), for C_4H_4 and Al_4Li_4 in Different Spin States Corresponding to Different Lowest Energy Structures

molecule	symmetry	spin state	energy	Δr
C_4H_4 [Figure 1A(i)]	D_{2h}	singlet	−154.718	0.240
C_4H_4 [Figure 1A(ii)]	D_{4h}	triplet	−154.708	0.000
Al_4Li_4 [Figure 1B(i)]	C_{2h}	singlet	−999.932	0.130
Al_4Li_4 [Figure 1B(ii)]	D_{2h}	singlet	−999.908	0.120
Al_4Li_4 [Figure 1B(iii)]	D_{4h}	triplet	−999.844	0.000
Al_4Li_4 [Figure 1B(iv)]	C_{2h}	triplet	−999.926	0.200

Since in Al_4Li_4 the $\sigma-\pi$ separation is poor, the Hückel π-electron picture is completely invalid. In fact, the π electrons in this case interact more strongly with the σ backbone and we expect a distorted structure as the ground state. The ground-state structure for the singlet state is found to be a rectangular Al_4 geometry with surrounding Li atoms, forming a C_{2h} symmetry group [Figure 1B(i)]. The same structure has been found in previous calculations as well.[6] Another low-energy structure in singlet manifold for Al_4Li_4 found by optimization is a diamond-shaped structure. It has a D_{2h} symmetry [Figure 1B(ii)] and is 15 kcal/mol higher in energy than the stable C_{2h} geometry [Figure 1B(i)]. Thus, the rectangular Al_4 ring in Figure 1B(i) corresponds to the ground-state geometry for Al_4Li_4. Similar to C_4H_4, the structural distortion in Al_4Li_4 leading to a magnetic triplet state with D_{4h} symmetry [Figure 1B(iii)] is found to lie 55 kcal/mol above the ground-state singlet [Figure 1B(i)]. There also exists a low-energy triplet structure with the same geometry as the ground state (C_{2h} symmetry) at an energy only 5 kcal/mol above the ground state. This triplet geometry [Figure 1B(iv)] for Al_4Li_4 does not have a counterpart in C_4H_4. This clearly demonstrates that, due to poor $\sigma-\pi$ separation in Al_4Li_4, there exist low-energy metallic states to accommodate the parallel arrangement of the electronic spins. The structural transition, however, does not occur involving this triplet geometry for Al_4Li_4.

Existence of a very stable rectangular ground-state structure together with a square geometry as the transition state for the Al_4 ring similar to those for C_4H_4 suggests that these inorganic clusters are antiaromatic in nature. This is expected since the highly electropositive Li atoms donate electrons to the Al atoms, thereby creating a species of the type Al_4^{4-}, π isoelectronic with C_4H_4. Thus we can safely consider Al_4Li_4 as a 4π-electron system with the π-HOMO (highest occupied molecular orbital) being a nonbonding molecular orbital as such as in C_4H_4. In the context of C_4H_4, Longuet-Higgins suggested that such a system can be stabilized if the nonbonding electrons form bonding molecular orbitals with suitable low-energy d orbitals of a transition metal. For this to happen, however, the energies of the d orbitals should lie close to the low-energy levels of the molecule alone. In the following, we propose a few stable complexes of Al_4Li_4 and compare their formation energies in comparison with their organic analogues.

$Fe(CO)_3$ Complex

A molecular complex, η^4-(C_4H_4)-$Fe(CO)_3$, has been recognized through the formation of such bonding molecular orbitals,

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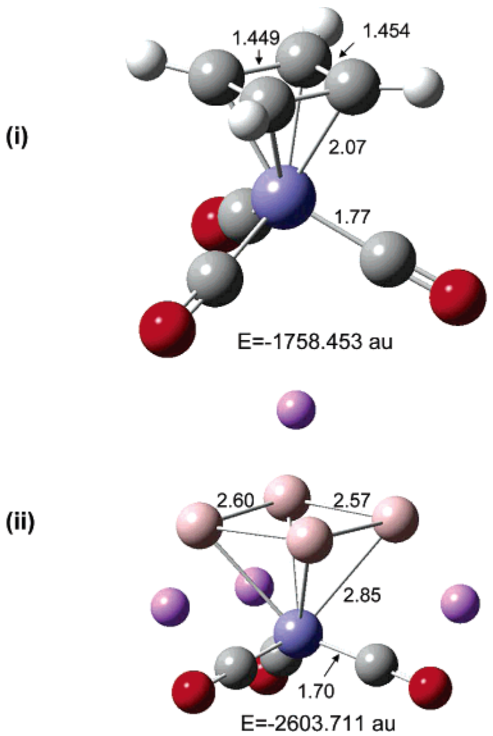

Figure 2. Equilibrium minimum energy geometries for (i) η^4-(C_4H_4)-Fe(CO)$_3$ and (ii) η^4-(Al_4Li_4)-Fe(CO)$_3$. Bond lengths are in Å. Ball color: red = O, violet = Fe.

and this complex has been reported to be quite stable.[16] In fact, oxidation of this complex releases the C_4H_4 ligand, which is a stable source for the highly reactive cyclobutadiene in organic synthesis.[17] For Al_4Li_4, we performed ground-state energy analysis on a similar system, η^4-(Al_4Li_4)-Fe(CO)$_3$, using the same level of theory mentioned above. Both η^4-(Al_4Li_4)-Fe(CO)$_3$ and its organic analogue have substantial stability (see Figure 2 for structures). Al_4Li_4 indeed forms a stable η^4 complex with Fe(CO)$_3$ [Figure 2(ii)]. The stability of the complexes are investigated using the following fragmentation scheme:

$$\eta^4\text{-}(C_4H_4)\text{-Fe(CO)}_3 = C_4H_4 + \text{Fe(CO)}_3$$

$$\eta^4\text{-}(Al_4Li_4)\text{-Fe(CO)}_3 = Al_4Li_4 + \text{Fe(CO)}_3$$

The binding energy for η^4-(Al_4Li_4)-Fe(CO)$_3$ is found to be 106.04 kcal/mol, while for η^4-(C_4H_4)-Fe(CO)$_3$ it is 78.44 kcal/mol. The comparable binding energies for the two compounds suggest that Al_4Li_4 is very well stabilized in the complex, in fact even more stabilized than C_4H_4. Note that compared to the ground-state structure for Al_4Li_4 where the Li ions are in interaction with the Al_4 ring, the structure for Al_4Li_4 in the complex gets deformed, losing all interaction with the Li ions. This amounts to a destabilization of 27 kcal/mol (calculated as the energy difference between the ground-state structure of Al_4Li_4 and the single point energy for the same in the η^4-(Al_4Li_4)-Fe(CO)$_3$ complex). The interaction of the Al_4 ring with the Fe(CO)$_3$ overwhelms the loss of interaction of Al_4 ring with the Li ions, stabilizing the overall structure of the complex.

The HOMO of the molecule (a nonbonding MO for C_4H_4) interacts with the low-energy d orbital of the ligand to form a bonding combination in the complex. Thus, C_4H_4 that initially possessed 4π electrons now has two more electrons, forming a species of the type $C_4H_4^{2-}$, an aromatic molecule. Similarly, for Al_4Li_4, the complexation converts it into $Al_4Li_4^{2-}$, a well-established aromatic complex.[4] The HOMO energies for C_4H_4 in the free form and in the coordinated form (derived by performing a single point energy calculation on the C_4H_4 fragment in the optimized complex) are −0.198 au and −0.157 au, respectively, while the same for the complex, η^4-(C_4H_4)-Fe(CO)$_3$, is −0.250 au. Similarly, for Al_4Li_4, the free and the coordinated forms have HOMO energies at −0.128 and −0.104, respectively, and the complex η^4-(Al_4Li_4)-Fe(CO)$_3$ has the same at −0.168 au. The stabilization of the frontier orbitals in the metal complex in both systems has its manifestation at the formation of the stable structure. The similarity in the difference between the HOMO energies of free and coordinated structures and with that of the corresponding complex for each molecule suggests that a similar mechanism is operative in lowering the energies of the frontier orbitals in stabilizing the respective complexes.

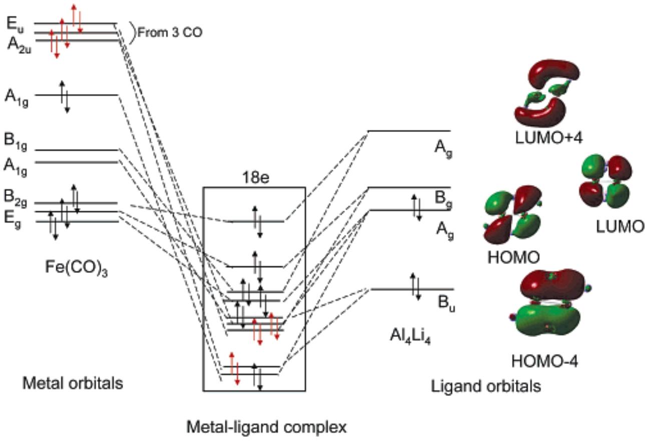

Figure 3. Orbital correlation diagram for η^4-(Al_4Li_4)-Fe(CO)$_3$. Only bonding orbitals are shown for sake of clarity.

For a clearer understanding of the qualitative similarities between C_4H_4 and Al_4Li_4 and its interactions with the Fe(CO)$_3$ fragment, we have analyzed the orbital correlation diagram for η^4-(Al_4Li_4)-Fe(CO)$_3$ in Figure 3. HOMO − 4, HOMO, LUMO, and LUMO + 4 orbitals have π character, while the other frontier orbitals (HOMO − 1, HOMO − 2) etc. have a σ-delocalized nature (see Supporting Information). The π orbitals of the metal cluster interact with the 3d transition metal orbitals to form a closed-shell 18-electron system, thereby stabilizing the η^4-(Al_4Li_4)-Fe(CO)$_3$ molecule, very similar to that derived earlier for stabilizing C_4H_4.[18] Note that there is donation of electrons from the Al_4Li_4 ring to the Fe d orbitals and the back-donation of electrons from Fe to the Al_4Li_4 ring, thereby making it a 6π-electron, aromatic system.

The above explanation is based on a simplistic picture of the interaction. To verify that indeed such a scheme is valid for a molecule with poor $\sigma-\pi$ separation like Al_4Li_4, we compare the Δr vlaues for both C_4H_4 and Al_4Li_4 in the free geometry and when they are complexed with the transition metal. For C_4H_4, the Δr is 0.24 Å in the free state. In the complex, η^4-(C_4H_4)-Fe(CO)$_3$, the Δr for the C_4H_4 ring is only 0.005 Å. Thus,

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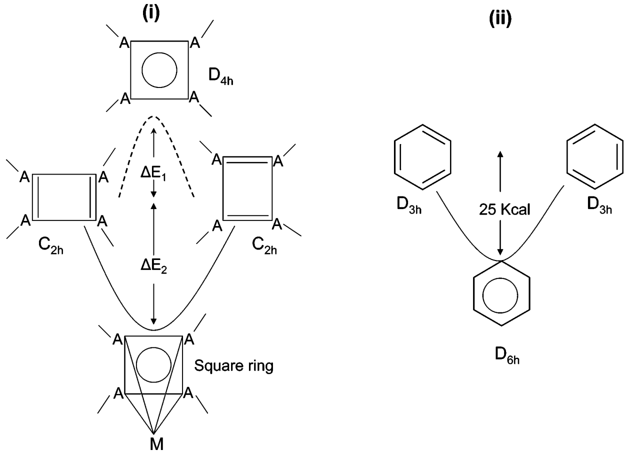

Figure 4. Schematic representation of (i) change in geometry for ring whizzing and complexation to transition metal center for A = Al in Al_4Li_4 (ΔE_1 = 55 kcal/mol, ΔE_2 = 100 kcal/mol); A = C in C_4H_4 (ΔE_1 = 6.2 kcal/mol, ΔE_2 = 78.4 kcal/mol). (ii) Ring whizzing in benzene.

C_4H_4 when complexed is a square rather than a rectangle, and as expected from the π-only interaction, it behaves as aromatic $C_4H_4^{2-}$. For Al_4Li_4, Δr = 0.13 Å in the free state while in the complex it is only 0.03 Å. This clearly supports that Al_4Li_4 has been converted into $Al_4Li_4^{2-}$, accounting for its substantial stability due to aromaticity. The complexation-induced metalloaromaticity in Al_4Li_4 is schematically shown in Figure 4. While a square (triplet) Al_4Li_4 is much higher in energy than the rectangular Al_4Li_4, this square form is stabilized on complexation to a transition metal. The same is the case for C_4H_4, where the square form becomes stabilized upon complexation. This is similar to the origin of aromaticity in benzene, where the π-delocalized D_{6h} structure corresponds to an energy minimum between two bond-altered Kekule forms with D_{3h} symmetry.

An even clearer picture is derived by performing a calculation for the nucleus-independent chemical shift (NICS)[19] at the GIAO-B3LYP/6-311+G(d,p) level. We calculate the NICS at the center of the Al_4 ring before and after complexation with the $Fe(CO)_3$. For comparison, the same values are also calculated for C_4H_4. In C_4H_4, NICS values before (C_4H_4) and after complexation ($C_4H_4^{2-}$) are 23.55 and −15.37 ppm, respectively. The change in sign clearly shows the transition from antiaromatic to aromatic nature upon complexation. For Al_4Li_4, the NICS values change from −11.01 ppm in the free state to −25.44 ppm on complexation in η^4-(Al_4Li_4)-$Fe(CO)_3$. The initial negative magnitude for NICS in free Al_4Li_4 supports the claim by Schleyer et al. that Al_4Li_4 has higher σ aromaticity than π antiaromaticity.[6] However, the increase in the NICS value with same negative sign suggests increased aromaticity in these clusters upon complexation, which is expected from the π-only picture of the conversion of Al_4Li_4 to $Al_4Li_4^{2-}$. Thus, complexation with $Fe(CO)_3$ induces metalloaromaticity in Al_4Li_4 and thereby stabilizes the complex, η^4-(Al_4Li_4)-$Fe(CO)_3$.

Bis(nickel(II) chloride) Complex

Next, we consider another very well-known example of a stable C_4H_4 complex, bis(cyclobutadiene nickel(II) chloride). The tetramethyl derivative for the complex crystallizes in a $P21/c$ point group and has a good resolution (R = 7.0%), CCD reference code NCBNIB.[20] We have obtained the structure from the database, and the methyl groups were substituted by H for easy comparison with the Al_4Li_4 derivative, bis(Al_4Li_4 nickel (II) chloride). Both structures, bis(cyclobutadiene nickel(II) chloride) and bis(Al_4Li_4 nickel(II) chloride), were optimized at the same level of theory as mentioned above. The structure for bis(cyclobutadiene nickel(II) chloride) remains similar to that found from the crystal structure. Figure 5 shows the structures for the two complexes. For the organometallic complex in Figure 5(i), the bond length alternation in the C_4H_4 ring is only 0.05 Å. Therefore, this bridged chlorine system also shows strong mixing of the d orbitals from Ni and the nonbonding electrons of C_4H_4.

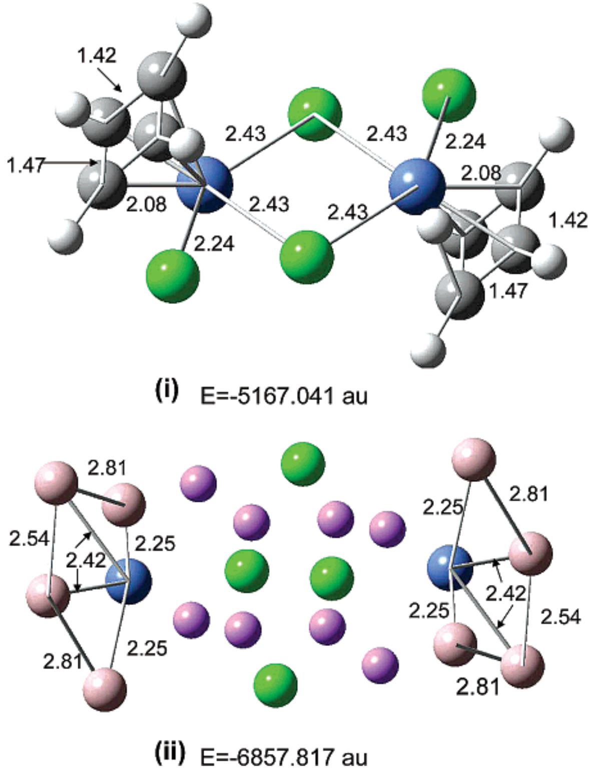

Figure 5. Equilibrium minimum energy geometries for (i) bis(cyclobutadiene nickel(II) chloride)and (ii) bis(Al_4Li_4 nickel(II) chloride). Distances are in Å. Ball color: green = Cl, blue = Ni.

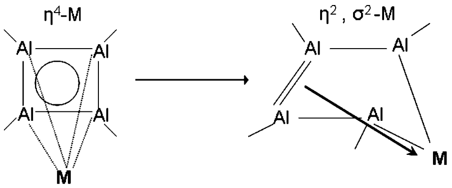

Figure 6. Conversion from η^4-binding mode for Al_4Li_4 to η^2,σ^2 in the complex in Figure 4(ii).

For the all-metal complex in Figure 5(ii), however, the η^4-(Al_4Li_4)-Ni binding mode is converted into η^2,σ^2-(Al_4Li_4)-Ni upon optimization. In Figure 6, we show this change in the binding mode. Two of the initial π bonds between Al and Ni (Al−Ni distance of the order 2.42 Å) are now converted into strong σ bonds (Al−Ni distance of the order 2.25 Å) in the optimized geometry. Such a change in bonding pattern from π

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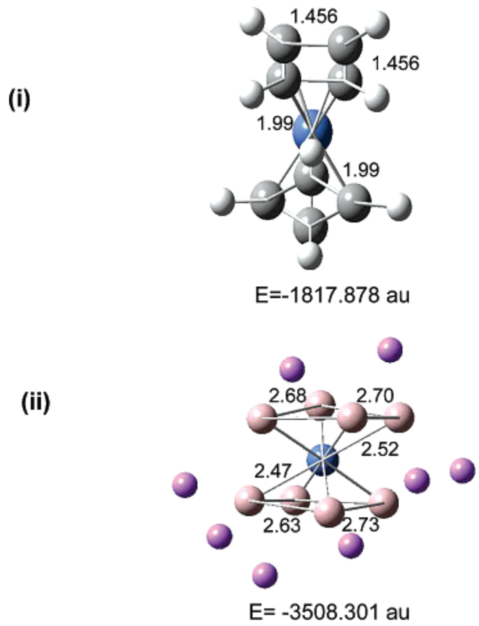

Figure 7. Equilibrium minimum energy geometries for (i) $(C_4H_4)_2Ni$ and (ii) $(Al_4Li_4)_2Ni$. Distances are in Å.

character to σ character is quite well-known in organometallic chemistry.[21] It is interesting to note that a similar phenomenon occurs in the all-metal complexes as well.

A fragmentation analysis on these two molecules is given by

$$\text{bis(cyclobutadiene nickel(II) chloride)} = 2C_4H_4 + \text{bis(nickel(II) chloride)}$$

$$\text{bis}(Al_4Li_4\ \text{nickel(II) chloride}) = 2Al_4Li_4 + \text{bis(nickel(II) chloride)}$$

The stabilization energies are 68.39 kcal/mol for Figure 5(i) and 286.77 kcal/mol for Figure 5(ii). Such high stability in the Al_4Li_4 complex is due to the formation of two strong Al−Ni σ bonds as discussed above. Similar to the case for η^4-(Al_4Li_4)-$Fe(CO)_3$, the interaction of the Li ions with the Al_4 ring in the bis(nickel(II) chloride) is completely lost.

Metal Sandwich Complex

Another well-known methodology in stabilizing a molecule is to form a sandwich type of geometry where two molecular species can share interaction with a transition metal: cyclopentadiene is stabilized in such a geometry, resulting in the ferrocene structure.[22] For C_4H_4, a simple effective electron number (EAN) counting shows that the metal between the two ligands should have 10 valence electrons in stabilizing a sandwich of the type $(C_4H_4)_2M$. The simplest metal with 10 electrons in the valence shell is nickel(0). Elements in the same group such as Pd or Pt have a strong spin−orbit coupling and prefer square-planar geometry (16-electron geometry). Thus, a coordination number of 8 as required in a sandwich complex is not possible with Pd or Pt. After performing the geometry optimization at the same level of theory discussed above, we find that the structure for $(C_4H_4)_2Ni$ is indeed a sandwich geometry with the two C_4H_4 rings above and below the Ni atom [see Figure 7(i)]. In this complex, the Ni atom sits symmetrically inside the cavity of the two C_4H_4 rings with a distance of 1.99 Å from each C_4H_4 ring. The two C_4H_4 rings are staggered from each other.

Similarly, we have been able to stabilize the Al_4Li_4 cluster by introducing it in a sandwich of the type $(Al_4Li_4)_2Ni$. The geometry is shown in Figure 7(ii) (the optimization and energy calculation at B3LYP/6-311G(d,p) level). The central Ni atom sits unsymmetrically in the cavity of the two Al_4Li_4 rings. A very recent theoretical study on its aromatic analogue, Al_4^{2-}, supports our calculations.[23] Interestingly, the Al atoms in the rings bend toward the Ni atom and the planarity of the Al_4 ring is thereby lost. This is understood from the fact that when the 4π electrons of each of the two Al_4Li_4 rings interact with the central Ni atom, the requirement of the Al atoms to be in plane with the Li atom is no longer important. Instead, the sandwich-like structure with 18 electrons gives an extra stabilization, keeping the whole system electrically neutral. The stability of these complexes is investigated using the following fragmentation scheme:

$$(C_4H_4)_2Ni = 2C_4H_4 + Ni(0)$$

$$(Al_4Li_4)_2Ni = 2Al_4Li_4 + Ni(0)$$

where Ni(0) is in a ^3F state. Al_4Li_4 binds strongly to the Ni(0) and has a binding energy of 146.054 kcal/mol. For C_4H_4 this binding energy is 150.819 kcal/mol. Note that, very similar to that in the other complexes discussed, metalloaromaticity is introduced for these sandwich complexes also.

In conclusion, we have demonstrated for the first time that all-metal species such as Al_4Li_4 can be stabilized by complexation with 3d transition metals, very similar to its organic counterpart, C_4H_4. Although such a complexation-induced metalloaromaticity is a well-established concept in the realm of organometallic chemistry, we have demonstrated that it is a very general and elegant concept that can be used for all metallic molecules with orbitals that are close in energy to the d orbitals of the transition metal. We have also shown that these all-metal complexes have binding energies and properties similar to those of their organometallic counterparts and thus should be considered as very good candidates for experimental synthesis. Also, such a stabilization will provide a very precise answer to the question of aromaticity/antiaromaticity and will lead to novel applications of these clusters. We believe that our work will motivate synthesis of these molecules as was the case in the previous generation for organometallic complexes.

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Supporting Information Available: Cartesian coordinates, total energy, frequency calculations for all structures. Spin contamination for triplet geometries and frontier orbital plot for ground-state structure of Al_4Li_4. This material is available free of charge via the Internet at http://pubs.acs.org.

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