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Assembly and Stabilization of a Planar Tetracoordinated Carbon Radical CAl_3Si: A Way To Design Spin-Based Molecular Materials

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Currently, spintronics[1] has attracted explosive interest. A key challenge is to transmit spin signals over long enough distances to allow for spin manipulation. To realize this goal, the spin of the designed molecules should be positively size-dependent (i.e., spin multiplicities linearly increase with the system size instead of the spin diminishment).[2] It is thus highly vital to inspect the spin evolution during the assembly and growth of molecular materials. Studies of a spin-based cluster assembly at a molecular level should shed insight into the macroscopic production of bulky magnetic materials. Thus, spin-controllable design, assembly, and manipulation will greatly advance the development of new functional materials and nanoelectronic devices.

Molecular species with spins are usually magnetic. One most interesting class of the spin-based materials[3] is the sandwichlike compounds that contain a transition metal center atom, for example, Cp_mTM_n[3a] and TM_nBz_m[3b−e] (Cp, Bz, and TM denote the cyclopentadienyl (C_5H_5), benzene (C_6H_6), and transition metal, respectively). Their ground-state spins are not governed by the closed-shell sandwich decks, but by the type of center atoms and by the interaction between the center TM-atom and the sandwich deck. Here we design a kind of spin-based magnetic molecular species based on an exotic planar tetracoordinated carbon (ptC) radical CAl_3Si. The spins of the newly designed molecular compounds are purely determined by the ptC radical (CAl_3Si)-decks.

The ptC realm has made vast progress in the past three decades.[4−5] Pentaatomic ptC species, first computationally designed[5a−b,g−i] and later experimentally observed,[5c−f] have attracted our particular attention. The simplicity of such species would make them find potential applications in the miniaturization race of components used in the construction of working devices.[6] Different from the traditional "top-down" fabrication approach, the new "bottom-up" approach allows the feasibility of assembling a small molecular unit into cluster to nanoscale to even bulk solid materials with special properties in our own will way.[6] Being the first smallest neutral ptC radical unit, CAl_3Si[5e−f] is taken for our model design for spin-based materials. A new scheme "*heterodecked sandwich*" (DMD* with D and D* being different decks) is proposed to capture and stabilize the planar radical based on the DFT-B3LYP /6-311+G(d)[7a−e] calculations. For the first time we show CAl_3Si to be a spin-embedded "superatom" for cluster-assembly. Our work represents the first attempt to bridge the ptC chemistry and spintronics realm.

Initially, the traditional "*homodecked sandwich*" form D_2M [charged $(CAl_3Si)_2M]^{q+}$ and neutral $(Cl^-)_q[(CAl_3Si)_2M]^{q+}$ with counterions Cl^- ($D = CAl_3Si$; M = Li, Na, K, $q = 1$; M = Be, Mg, Ca, $q = 2$) are considered. Charged sandwich isomers are not the ground state structure, whereas neutral sandwich isomers do not exist at all. So, the ptC radical CAl_3Si cannot be assembled in the traditional homodecked sandwich scheme.

Alternatively, we propose a new scheme "heterodecked sandwich" to assemble CAl_3Si in forms of D*MD (D* = rigid decklike Cp^-, $D = CAl_3Si$). In general, there are three kinds of sandwich forms $\mathbf{1}^{q+}$**(f-f)**, $\mathbf{1}^{q+}$**(f-s)**, and $\mathbf{1}^{q+}$**(f-c)** (Figure 1). For neutral $CpM(CAl_3Si)$ (M = Li, Na, K), charged $[CpM(CAl_3Si)]^+$ (M = Be, Mg, Ca), and charge-compensated $(Cl^-)[CpM(CAl_3Si)]^+$ (M = Be, Mg, Ca), the sandwich structure is the ground-state isomer.[8,9] Thus, the ptC radical CAl_3Si can effectively sandwich metal atoms in cooperation with a rigid decklike Cp^-.

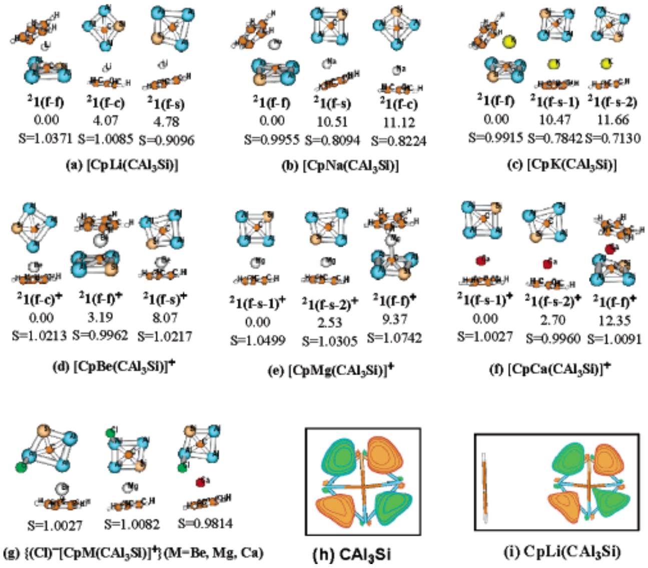

Figure 1. Sandwich forms $CpM(CAl_3Si)$ (M = Li, Na, K), charged $[CpM(CAl_3Si)]^+$ (M = Be, Mg, Ca), charge-compensated $(Cl^-)[CpM(CAl_3Si)]^+$ (M = Be, Mg, Ca) and the HOMO orbital diagrams[10] of CAl_3Si and $CpLi(CAl_3Si)$] at the B3LYP/6-311+G(d) level. Energy values are in kcal/mol. "*S*" denotes the spin density of the CAl_3Si unit.

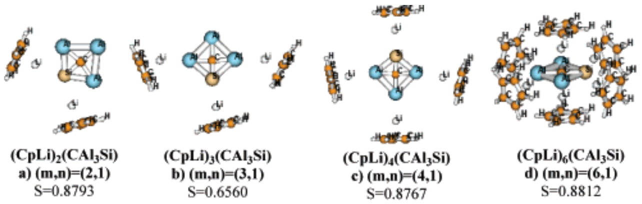

Figure 2. Some extended sandwich complexes of $(CpLi)_m(CAl_3Si)_n$ with $(m,n) = (2,1)$, $(3,1)$, $(4,1)$ at the B3LYP/6-31+G(d) level and $(6,1)$ at the B3LYP/3-21G level.

Some metallocenes are known to form highly extended sandwich complexes ranging from nanoscales to polymers, and even to bulk solid materials.[3a] We further designed the ptC-based extended systems containing more Cp^- units in various heterodecked sandwich forms, some of which are shown in Figure 2. Surely, the growth from the simple extended sandwich structures to the much more highly extended 3D sandwich networks with more Cp^- and CAl_3Si units is very viable. For computational reason, we did not attempt to calculate these species.

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From Figures 1 and 2, we can see that the structural and electronic integrity of CAl_3Si and its characteristic HOMO orbital are generally well kept during the heterodecked sandwiching. Also, the spin density ("*S*" values in Figures 1 and 2) of the CAl_3Si unit within the assembled compounds nearly amounts to 1 as in the free CAl_3Si radical, suggestive of the good spin-conservation. Moreover, the positive and negative charges are dominantly positioned at the M-atom and Cp unit, respectively, indicating the major molecular formula $(Cp^-)M^q(CAl_3Si)$ ($q = +1$ for Li, Na, K and $q = +2$ for M = Be, Mg, Ca).[11] Thus, the spin-embedded planar radical CAl_3Si could act as a new type of "superatoms".[12] To our knowledge, this is the first time to consider a neutral planar radical as a superatom. Future studies on the superatom chemistry of CAl_3Si radical are desired.

The capture and stabilization of radicals has continued to be a great challenge to chemists. Generally, radicals are very reactive and their stabilization has to be gained through "steric-stabilization" by using bulky substitutions within the molecular skeleton (e.g., $C(CH_3)_3$). Yet, they cannot be used as building blocks in cluster assembly because of their bulkiness. The present target radical CAl_3Si has an interesting planar ptC-center. The spins are evenly distributed over the peripheral four atoms, suggesting that each of the peripheral atoms is apt to react with outer reagents. Luckily, our newly proposed heterodecked sandwich scheme can effectively suppress the reactivity of CAl_3Si by introducing the neutral LiCp pairs (see Figure 1 and 2). It is even possible that the reactivity of CAl_3Si can be completely suppressed by being fully "dressed" with six LiCp pairs (see Figure 2d) in six directions. In this way, the ptC CAl_3Si radical is well captured into a "rice-ball" structure (Figure 2c) and a "cage" structure (Figure 2d). We call such a radical-stabilization method "sandwich-stabilization". The advantages of the new method are that (1) the steric effect can easily be introduced by choosing suitable "dressers" (e.g., change LiCp to LiCp* with all H-atoms substituted by methyl groups), (2) the neutral LiCp pairs can be facilely "undressed" when we want to have CAl_3Si for further usage, and (3) thus, the manipulation of spins should be easy by simply capturing more ptC CAl_3Si radicals dressed by LiCp pairs.

The easy capturability by our newly proposed heterodecked sandwich scheme and the spin-embedded superatom feature lead us to predict that the ptC radical CAl_3Si can act as a spin-embedded cluster building block to design magnetic molecular materials. The unpaired spins of the designed clusters should linearly increase with the number of CAl_3Si units. The bulky LiCp pairs should well separate the CAl_3Si-decks from each other, resulting in the effective avoidance of fusion. Thus, our designed heterodecked sandwich and proposed nanoscale highly extended sandwich species would be ideal materials for promising spin-polarized transport.

In summary, the present study described the first attempt to assemble and stabilize a neutral ptC radical CAl_3Si via our newly proposed heterodecked sandwich scheme. The new scheme is testified to be an effective way to capture planar radicals and to design spin-based molecular materials. Such capture and assembly procedures could also be applied to many other planar radicals, such as CAl_3Ge, XAl_4^{q-} ($q = 0, 1$; X = Al, Si, Ge), and NAl_4, etc. In particular, the feature that the sandwich stabilizes the ptC radical CAl_3Si itself should play an important role in spin-controllable design, assembly, and manipulation of materials. A rich realm of spin-controllable design, assembly, and manipulation will be foreseen, which will greatly advance the development of new functional magnetic materials and nanoelectronic devices in the era of spintronics. Such linkage might lead to unique phenomena or even gestate a field.

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Supporting Information Available: Complete ref 7, structural properties, and spin densities. This material is available free of charge via the Internet at http://pubs.acs.org.

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