

Small metal–organic molecular sandwiches: Versatile units for induced structure manipulation



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ABSTRACT

Interfaces between metal atoms and organic molecules are key units of many important metal–organic systems. Presented are results of ab initio calculations for a series of complexes of 2nd-row metal atoms sandwiched between small unsaturated hydrocarbon molecules. Evolution of the system structure and stability is studied for different metal atoms, as well as upon excitation, ionization and electron attachment. Predicted interesting features include cooperative stabilization, unusual geometries, reversible charge- or excitation-governed geometry alterations. The observed variety of properties suggests potential applications of such species as intermolecular junctions and units with charge- or spin-controlled shapes in molecular devices and/or machines.

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1. Introduction

Metal–carbon interfaces at molecular level have many practical applications including, in particular, composite nanomaterials, catalysis, electronics and photonics. For example, metal atoms and clusters supported on graphite, graphene, carbon-nanotube and similar substrates can provide new catalytic properties or, alternatively, modify characteristics of the host via doping. Also, direct metal–carbon junctions may offer a better performance in terms of conductance or other relevant effects (photo-induced processes, etc.) in molecular electronic devices. The list could also be extended to metal atoms/clusters inside the nanotubes, fullerenes, etc.

Smaller-size examples involve various metal–organic complexes up to the case of a single ligand. In particular, recently such and larger systems have been considered also from the viewpoint of hydrogen storage, via adsorption of H_2 molecules to metal atoms attached to unsaturated hydrocarbon species, mainly with double C=C bonds such as in C_2H_4 and C_5H_5 [1,2]. In addition to the commonly known metallocenes $M-(C_5H_5)_2$ and metallobenzenes $M-(C_6H_6)_2$, analogous ‘sandwich’ systems of a pair of smaller molecules, e.g. C_4H_6 (butadiene) and C_2H_4 , separated by a metal atom [3,4] are further illustrations of metal–carbon molecular interfaces. These species can be viewed as examples of metal-mediated junctions between molecules. Such junctions are of interest as means of connecting molecular components in a way potentially enabling design of the shapes and properties of resulting assemblies and nanostructures, thus expanding the variety of metal–organic frameworks. Moreover, such systems could possibly allow for a

controlled modification of their geometries and characteristics via electronic perturbations.

Most of the above systems involve transition metal atoms, with relatively few examples of main-group counterparts, such as $M = Li$ and Be [5,6]. In a previous study [7], minimal interfaces between two ethylene molecules mediated by $M = Be$ and Mg have been considered. The Be -based species have demonstrated a strongly (non-additively) increased stabilization as compared to $Be-C_2H_4$, similar to the analogous cooperativity of binding for other ‘sandwich’ versus ‘half-sandwich’ systems mentioned above. In addition, $Be-(C_2H_4)_2$ have exhibited a considerable reversible geometry change upon electronic excitation. The present Letter investigates and compares a few representatives of this family, employing the main-group 2nd-row metals surrounding Be in the Periodic Table. Furthermore, of direct interest here is to actually track the alterations of the system structures upon ionization, electron-attachment, and electronic excitation as possible inductors of the structure manipulation. Besides, upon ionization the cooperativity of binding was lost for the $Li-(C_6H_6)_2$ as well as $Ni-(C_4H_6)_2$ cases [5,3]. A related purpose of the present Letter is to check how ionization and electron attachment affect this feature for smaller ‘sandwiches’.

2. Computational procedure

All calculations have been carried out at the MP2 (2nd-order perturbation theory) level with standard aug-cc-pVXZ basis sets [8], as implemented in the NWChem ab initio software [9]. Basis set superposition error (BSSE) correction has been applied via a common counterpoise procedure [10].

Unrestricted (C_1 symmetry) optimization has been performed in each case from several suitable geometries, and minima of

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energy confirmed via all-real vibrational frequencies. Single-point aug-cc-pVQZ energies have been obtained for the aug-cc-pVTZ geometries. The ground state multiplicities have been checked by calculations for higher-spin states as well. Atomic charge distributions have been evaluated using the natural bonding orbital formalism [11].

As a test, using the above level of theory, the dissociation energy of the BC diatom is calculated to be 4.46 (4.38) eV without (with) the BSSE correction, both values falling within the experimental interval of 4.6 ± 0.3 eV [12]. In addition, the predicted ionization energies of 5.36 eV (Li), 8.87 eV (Be), 8.31 eV (B) compare well to, respectively, 5.39, 9.32, 8.30 eV from experiments [13].

3. Results and discussion

In agreement with the earlier works, all studied $M-C_2H_4$ species have stable isomers with the M atom lying in the symmetry axis perpendicular to the (initial) plane of the molecule, with the C–H bonds bending away from the atom (Figure 1), consistent with a partial re-hybridization of the C atoms (from sp^2 to sp^3) upon bonding to M. The stability to dissociation to $M + C_2H_4$ increases dramatically from $M = Li$ to B (Table 1). This can be related to the decreasing size of the atom from Li to B (allowing a closer approach) and to the increasing contribution of the bonding-facilitating 2p-orbital in M (enabling larger overlap), which is empty in isolated Li, occupied in isolated B and being readily populated in Be due to its sp -hybridization in the system. Bonding of σ and π type involving atomic p-orbitals and molecular π -orbitals has been detailed, in particular, for $Al-C_2H_4$ [14]. The $Li-C_2H_4$ system is bound weakly, in agreement with previous work [15], and in fact comparably to its other, van der Waals isomer with a flat ethylene molecule farther away from the lithium atom, which type of systems is not a focus of the present study. The break of the π -bond in C_2H_4 , consistent with stretching C–C bond, is thus just compensated by the Li–C bonding, while the M–C bonding strengthens considerably for $M = Be$ (see also previous work [7]) and B. In particular, the calculated $B-C_2H_4$ binding energy is close to 2.01 eV found earlier [16]. Both bending of the ethylene molecule in $M-C_2H_4$ and the C–C bondlength peak for $M = Be$. The equilibrium M–C distances decrease from $M = Li$ to B, thus varying opposite to the binding energies, as expected. Even though the insertion of B between two C atoms is predicted to lead to a lower-energy isomer, this is beyond our consideration due to the corresponding high potential barrier of about 3 eV [16].

Addition of a second ethylene molecule on the opposite side of the metal atom stabilizes the $M-(C_2H_4)_2$ ‘sandwich’ considerably for $M = Li$ and Be, two molecules exhibiting a strong cooperativity of binding with much more than double dissociation energy as compared to $M-C_2H_4$ (Table 1). These systems show a parallel arrangement of the ethylene units, slightly distorted for $M = Li$, with both molecules at equal distances from M (Figure 2). Cooperative binding has also been found for $Li-(C_6H_6)_2$ [5]. The situation is different for $M = B$, with the molecules binding anti-cooperatively, i.e. with the 2nd molecule bound more weakly than the 1st one. For this system two equidistant C_2H_4 units are twisted

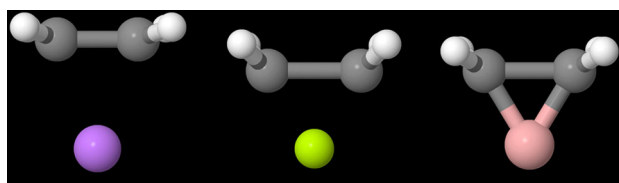


Figure 1. Optimized geometries of $M-C_2H_4$, $M = Li, Be, B$.

Table 1

Equilibrium parameters (in eV, Å, and degree) of $M-C_2H_4$ and $M-(C_2H_4)_2$ and their ions.

System ^a	D_e^b	R_e (M–C)	R_e (C–C)	Θ_e (HCCH)
$Li-C_2H_4$	0.21 (0.06)	2.04	1.42	155
Cation	1.01 (0.91)	2.34	1.34	176
Anion	–0.49 (–0.66)	1.99, 2.00	1.48	138
$Li-(C_2H_4)_2$	0.88 (0.66)	2.13	1.37	171
Cation	1.87 (1.70)	2.36	1.34	176
Anion	0.73 (0.49)	2.07	1.43	150
$Li-C_4H_8^c$	0.44 (0.27)	2.00, 2.35	1.48–1.53	
Cation	2.33 (2.13)	2.09, 2.15	1.54, 1.58	
Anion	1.58 (1.36)	2.02	1.54	
$Be-C_2H_4$	0.49 (0.34)	1.61	1.65	126
Cation	1.66 (1.55)	1.73	1.45	156
Anion	1.22 (1.14) ^d	1.70	1.56	128
$Be-(C_2H_4)_2$	2.71 (2.49)	1.75	1.43	155
Cation	4.53 (4.35)	1.84	1.39	168
Anion(p)	2.48 (2.35) ^d	1.70, 1.90 ^e	1.57, 1.43 ^e	127, 159 ^e
$B-C_4H_8^c$	3.72 (3.55)	1.67	1.55, 1.56	
Cation	3.49 (3.34)	1.65, 1.86	1.50–1.56	
Anion	3.68 (3.58)	1.75	1.53	
$B-C_2H_4$	2.61 (2.48)	1.52	1.57	138
Cation (i)	3.55 (3.39)	1.43	2.85	
Anion	3.08 (2.95)	1.60	1.52	141
$B-(C_2H_4)_2$ (t)	4.70 (4.47)	1.59	1.48	146
Cation	6.68 (6.44)	1.60	1.44	159
Anion (p)	6.59 (6.39)	1.57	1.55	133
$B-C_4H_8^c$	5.45 (5.30)	1.56	1.53, 1.54	
Cation	7.20 (7.04)	1.47	1.57, 1.59	
Anion	5.34 (5.19)	1.61	1.52, 1.54	

^a Geometry notations: (p) C_2H_4 units are perpendicular to one another, (t) twisted at an angle (parallel being default), (i) with M inserted between the C atoms; Θ_e (HCCH) is the dihedral C_2H_4 folding angle about the C–C axis.

^b Values in brackets are BSSE-corrected.

^c Cyclic isomer.

^d Relative to neutral Be and C_2H_4 products.

^e for C_2H_4 farther away from M.

at an angle of about 54° to one another. This is consistent with the B atom being an electronic intermediate between Be and C, the latter corresponding to spiropentane C_5H_8 which has analogous $C-(C_2H_4)_2$ structure with a perpendicular orientation of the ethylene units. Such a geometry of $B-(C_2H_4)_2$ also resembles that of iso-electronic $C-(C_2H_4)_2^+$, as obtained in additional calculations at the same level of theory.

In all $M-(C_2H_4)_2$ systems the ethylene molecules are farther away from the metal atom and less bent as compared to the $M-C_2H_4$ species (Table 1), for $M = Li$ and Be in spite of the increased binding. The M–C distances and dissociation energies show the same relative variations with M as for $M-C_2H_4$, while the C–C bondlength increases monotonically with the M size, different from the situation for $M-C_2H_4$.

In all systems, the metal atom is positively charged, for $M = Be$ about twice as much as for $M = Li$ and B (Table 2). From $M-C_2H_4$ to $M-(C_2H_4)_2$, however, this charge changes relatively weakly for $M = Li$ to B, hence each ethylene unit is charged about twice less in $M-(C_2H_4)_2$. All $M-C_2H_4$ are considerably polar, and the slight asymmetry of $Li-(C_2H_4)_2$ also results in a small dipole moment.

The ground states of all systems are found to have the lowest possible multiplicity, singlet for $M = Be$ and doublet for Li, B. The electronic excitation to a higher spin state (triplet for Be and quartet for the other M) destabilizes the systems. Open-shell $M-(C_2H_4)_2$ become metastable, with energy of about 1–2 eV (for $M = Li$ and B) above that for separate $M + 2 C_2H_4$. For the $M = B$ case there even appears a ‘cooperativity of destabilization’, since $B-C_2H_4$ is destabilized much less as compared to $B-(C_2H_4)_2$. The $Be-(C_2H_4)_2$ sandwich remains bound, with the binding energy reducing to

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