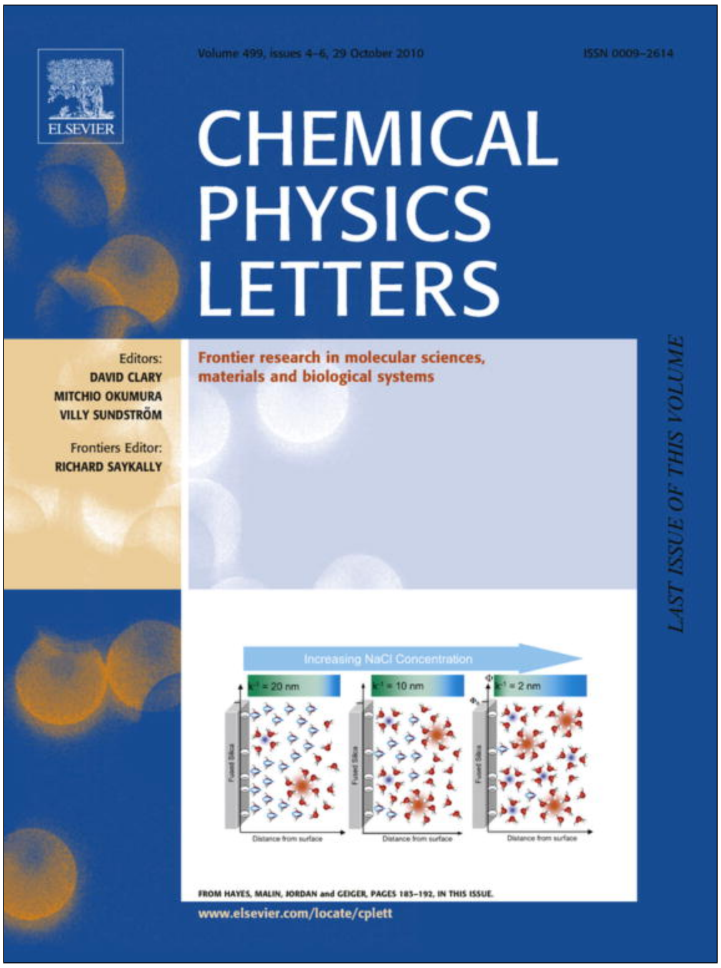
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Complexes of Be and Mg with unsaturated hydrocarbon molecules: Inter- and intramolecular cooperativity of binding

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ABSTRACT

Ab initio calculations are employed to investigate attachment of Group II light metal atoms to hydrocarbon molecules with pairs of double carbon–carbon bonds. Comparison of the atom attachment to one and between two such bonds reveals cooperative binding for some cases, with some counter-intuitive features. Dependence of its manifestation on the system composition and geometry is investigated for a series of metal–hydrocarbon complexes. Attachment-induced catalytic isomerisation of the system is considered at molecular level as well. The complexes are characterized and compared in terms of geometry, stability and various electronic properties.

1. Introduction

Attachment of metal atoms to polyatomic carbon-based species can occur in various forms. These include ‘surface doping’ of graphite (with a natural extension to graphene), as well as functionalization of fullerenes and carbon nanotubes (including both exo- and endohedral doping). The widest variety of complexes of transition metal atoms with organic molecules are smaller-scale representatives of such systems, at molecular level, review of which numerous species is, however, beyond the scope of the present work.

Among a huge multitude of the complexes, those of main-group and transition metal atoms with even the smallest unsaturated hydrocarbons such as acetylene and ethylene exhibit some interesting features in binding. These include (1) strong variations in the metal–molecule bond strength for different systems – from weak for, e.g., Mg–C_2H_2 [1] and Li–/Na–/K–C_2H_4 [2] to significant (~1 eV or more) for, e.g., Be–C_2H_2 [3], Fe–C_2H_2 [4], Ni–C_2H_4 [5] and Ti–/Zr–/Hf–C_2H_2 [6]; (2) relative stability of isomers – with two attached molecules remaining separate (e.g., in $Ni(C_2H_4)_2$ [7]) as compared to their fusion (as in $Mg(C_2H_4)_2$ [8] and $Fe(C_2H_2)_2$ [4], and possible reversal of this order for metal ions (e.g., for $Ni^+(C_2H_2)_2$ [9]); (3) cooperativity of binding – with the total bond strength more than doubling on attaching a 2nd identical molecule even without fusion (as for $Fe(C_2H_2)_2$ [4]), and possible opposite situation for ionic systems (e.g., for $Ni^+(C_2H_2)_2$ [10]). The latter cooperativity is known also for larger counterparts including, in particular, benzene complexes with some transition metals (e.g., $V(C_6H_6)_2$ [11]). It is found to be significant for some unsaturated molecules other than hydrocarbons as well (e.g., in $Fe(CO)_2$ [12,13]), while may diminish in the corresponding ions (e.g., $Fe(CO)_2^+$ [14,15]).

The purpose of the present work is to investigate complexes of main-group light metal atoms (M = Be, Mg) attached to unsaturated hydrocarbon molecules with pairs of carbon–carbon double bonds. Such complexes have not been studied previously, to the best of the author’s knowledge. Unlike transition metals, the Group IIA atoms have closed valence subshells (ns), and previous work on their (especially Be) complexes with organic molecules is relatively scarce (with relevant references given later in this Letter). Specific aspects of interest here include generality of cooperative binding – especially for both C=C bonds belonging to the *same* molecule, as well as metal-atom attachment induced alteration of the molecular structure and associated variations of other properties of the systems. Potential future applications include prediction of preferential attachment sites for metal atoms on organic molecules and design of stable metal–organic molecular interfaces, metal-atom catalyzed isomerisation of molecules and manipulation of their structural and related parameters.

2. Computational procedure

The systems of interest are covalently bonded isomers with anticipated significant charge transfer as well as those bonded weakly. Taking into account also the appreciable size of the molecular components composed of up to eight carbon atoms, the MP2 level of theory is preferred. Geometry optimization is carried out with the aug-cc-pVTZ basis sets on all atoms, followed by a single-point energy calculation with the aug-cc-pVQZ basis sets [16]. The basis-set superposition error is corrected using a standard (counterpoise) procedure. All calculations are carried out by means of the NWChem ab initio package [17].

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Multiple initial geometries are employed for each system, in order to locate different isomers. Since the primary purpose is investigation of metal atom attachment, the starting configurations are limited to those of intact molecules approached by the metal atom, with no insertion of it into their C–H bonds. Unconstrained all-atom optimization is performed for each case, followed by vibrational frequency analysis to confirm energy minima. Higher-spin states are also evaluated, in particular to aid verification of the ground state multiplicity. Natural charges are employed to describe charge distributions over atoms.

3. Results and discussion

3.1. M–C_2H_4 and M$(C_2H_4)_2$

The weakly bound Be...C_2H_4 complex is found to have equilibrium distance of the Be atom ≈3.7 Å away from the center of the molecule, while this distance is 1.38 Å for the covalently bonded isomer with a C_{2v} structure (Figure 1) resembling that predicted earlier [18]. However, while that previous (also MP2) calculation has indicated dissociation energy of only ≈0.05 eV, i.e. comparable to the weakly bound system, the present value is an order of magnitude larger (Table 1), likely due to larger basis set. The significant stretch (by ≈0.3 Å) of the C–C bond and non-planarity of C_2H_4 in the covalently bonded complex indicates Be–C bonding at the expense of the C–C π-bond. The triplet state is slightly higher in energy (Table 2), being almost unbound (essentially metastable, with $D_e \approx 0$) relative to Be + C_2H_4, with less distorted (shorter and more planar) ethylene molecule ≈0.3 Å farther away from Be.

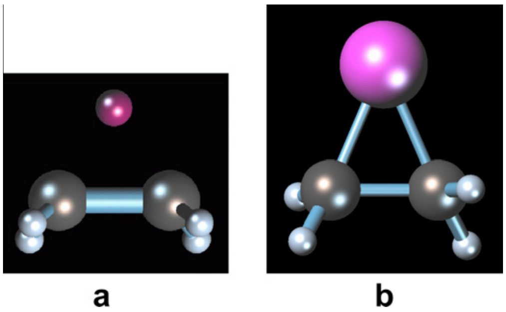

Figure 1. Optimized structure of singlet Be–C_2H_4 (a) and Mg–C_2H_4 (b). All pictures in this work are generated using the ViewMol3D software, http://redandr.tripod.com/vm3/.

By comparison, for Mg–C_2H_4 the covalently bonded structure is metastable, with energy above dissociated Mg + C_2H_4 (Table 1). The Mg–C bonds are longer and C–C shorter than in Be–C_2H_4. Moreover, the lower-energy state is triplet (Table 2), while the singlet state has a twisted (around the C–C bond) ethylene unit with staggered C–H bonds (Figure 1), both features unlike for Be–C_2H_4. The quintet state is ≈4 eV above the ground state. Both the above metastability and energy-order of spin states resemble the corresponding properties of Mg–C_2H_2 [3].

Addition of a 2nd ethylene molecule on the opposite side of the Be atom (Figure 2) stabilizes the resulting symmetric C_2H_4–Be–C_2H_4 system dramatically, with the total binding energy increasing by an order of magnitude (Table 1), thus exhibiting a very strong cooperativity. This could possibly be associated, at least in part, with the 2s subshell of the Be atom already open (and sp-hybridization in Be initiated) by attaching the first molecule. By comparison, no significant stabilization is found, e.g., for Ga–$(C_2H_4)_2$ as compared to Ga–C_2H_4 [19], consistent with the valence p subshell already open in isolated Ga atom and with its likely sp^2 hybridization on attachment of the 2nd molecule (in accord with its position near rather than opposite the 1st one). A somewhat counter-intuitive feature is that, compared to Be–C_2H_4, each C_2H_4 unit in C_2H_4–Be–C_2H_4 is slightly further away (by ≈0.1 Å) from Be and is less distorted (flatter and with ≈0.2 Å shorter C–C bond). Such a Be–C bond stretch could be related, e.g., to repulsion of charges as well as induced dipoles on two attached molecules. The triplet state is significantly higher above the ground state (Table 2) as compared to Be–C_2H_4, while remaining significantly bound relative to Be + 2 C_2H_4. Interestingly, it has the C_2H_4 units turned perpendicular to one another while slightly further away from Be. By comparison, a similar twisted geometry was found for the singlet ground state of Ni–$(C_2H_4)_2$ [7].

A potential barrier separates the above C_2H_4–Be–C_2H_4 isomer from the cyclic Be–C_4H_8 one (Figure 2), with two ethylene molecules converged around the Be center and fused via a new C–C bond, formation of which is, in effect, catalyzed by the metal atom. Similar situation is found for Ga–$(C_2H_4)_2$ [19] and Fe–$(C_2H_2)_2$ [4]. The Be–C_4H_8 system is ≈1 eV lower in energy (Table 1), with three C–C bonds of near-equal lengths zig-zagging around and forming a cycle with the metal atom, each C_2H_4 unit being twisted around its

Table 1
Equilibrium parameters (in eV and Å) of metal–hydrocarbon systems (M = metal, in brackets are triplet state values).

System		D_e	R_e(M–C)	R_e(C–C)
Be–C_2H_4		0.34	1.61 (1.83)	1.65 (1.42)
Mg–C_2H_4		−2.11	2.02 (2.25)	1.60 (1.42)
C_2H_4–Be–C_2H_4		2.49[a]	1.75 (1.82)	1.43 (1.43)
BeC_4H_8		3.55[a]	1.67 (1.73, 2.27)	1.55–1.56 (1.48–1.52)
MgC_4H_8		1.02[a]	2.07 (2.15, 2.60)	1.54–1.55 (1.48–1.52)
Be–C_6H_6	central	0.72	1.79 (2.00)	1.44 (1.39)
	side	0.71	1.61	1.72[b], 1.35[c]
Mg–C_6H_6	side	−1.69	2.03	1.67[b], 1.35[c]
Be–C_8H_8	central	1.63	1.77 (1.69–1.82)	1.45 (1.45–1.48) 1.74[b]
	side	0.59	1.61	1.35[c]
	fused	1.93	1.67 (1.72, 2.29)	2.68[b], 1.56[d] (2.58[b], 1.50–1.55[d])
Mg–C_8H_8	fused	−0.35	2.08 (2.15, 2.58)	2.82[b], 1.54[d] (2.65[b], 1.50–1.54[d])
	side	−1.90	2.03	1.68[b], 1.35[c]
Be–C_8H_{12}	central	1.62	1.75–1.76 (1.96–1.98)	1.45 (1.38)
	side	0.18	1.61	1.68[b], 1.34[c]
Mg–C_8H_{12}	central	−1.65	2.16–2.18 (2.36–2.41)	1.45 (1.38)

[a] Into M + 2 C_2H_4.
[b] For the C–C bond facing M.
[c] For the C=C bond on the other end of the 'ladder'.
[d] For the 'former C=C' bonds (to the atoms facing M).

Table 2
Energies, atomic charges, and dipole moments (in eV, e, and D) of metal-hydrocarbon systems (M = metal, in brackets are triplet state values).

System		E* (S = 0 → 1)	q(M)	μ	VEA	VIE
Be–C_2H_4		0.32	1.40 (0.76)	1.95 (1.47)	0.55	8.82
Mg–C_2H_4		−1.00	1.25 (0.77)	4.46 (0.40)	1.13	7.30
C_2H_4–Be–C_2H_4		1.12	1.56 (1.46)	<0.1	<0	7.38
BeC_4H_8		2.99	1.44	0.73	<0	9.73
MgC_4H_8		1.71	1.39	3.02	0.40	7.90
Be–C_6H_6	central	0.51	1.51	1.42	<0	6.70
	side		1.38	1.71	0.59	8.93
Be–C_8H_8	central	1.71	1.55	0.78	<0	7.12
	side		1.39	1.45	0.55	8.52
	fused	2.61	1.42	0.62	0.19	8.58
Mg–C_8H_8	fused	1.5	1.27	2.82	0.48	7.39
Be–C_8H_{12}	central	1.23	1.56	1.01	<0	7.00
	side		1.39	1.69	0.39	8.53
Mg–C_8H_{12}	central	−0.59	1.54	3.60	0.22	6.92

C–C bond and making a staggered arrangement of C–H bonds. On removal of Be (or detachment of C_4H_8 from it), cyclobutane is formed, with D_e(Be–C_4H_8) = 2.31 eV. Compared to the C_2H_4–Be–C_2H_4 isomer, the triplet state of Be–C_4H_8 is about 3 times higher in energy relative to singlet (Table 2), with Be shifting closer to one of the terminal C atoms of C_4H_8.

By comparison, the analogous C_2H_4–Mg–C_2H_4 structure corresponds to a transition state still (though much less compared to Mg–C_2H_4) higher in energy than the dissociation limit. This could be related to the open-shell character of Mg–C_2H_4 discussed above. Further relaxation leads to the MgC_4H_8 cyclic isomer (also identified earlier [8]) stable to dissociation into Mg + 2C_2H_4 (Table 1). The negative value of D_e(Mg–C_4H_8) = −0.21 eV would favor catalytic fusion of two ethylene molecules into cyclobutane on the Mg atom (unlike on Be) if metastable Mg–C_2H_4 could form and live long enough to react with the other C_2H_4. The triplet-singlet gap for MgC_4H_8 is about half that for BeC_4H_8 (Table 2) the triplet state being higher in energy than Mg + 2C_2H_4.

3.2. M–C_6H_6 and M–C_8H_8

There are many larger molecules with a few carbon–carbon double bonds in each, which could exhibit cooperative binding to metal atoms within the same molecule. A recently studied case has involved butadiene C_4H_6 which can be viewed as two C_2H_4 units fused together (with two H atoms removed). Each such molecule is found [20] (with DFT) to bind to Ni atom about twice as strongly as ethylene does, i.e. with no cooperativity for two C═C bonds located on the same side of metal atom. Still, two C_4H_6 molecules on the opposite sides of Ni do exhibit cooperative binding, with energy significantly more than double that for Ni–C_4H_6. And again, this feature is lost for Ni^+.

Among other hydrocarbons, each of bicyclo [2.2.0] hexa-2,5-diene C_6H_6 and tricyclo[4.2.0.0^{2,5}]octa-3,7-diene C_8H_8 [21] have a pair of parallel C═C bonds at the opposite ends of bent ladder-like structures, suitable for trapping a metal atom in-between. To evaluate the cooperativity of binding, two isomers are compared: one with the metal atom captured between the two C═C bonds, and the other one with this atom on the side of the molecule, attached to the nearest C═C bond. Both Be–C_6H_6 and Be–C_8H_8 complexes also exhibit weakly bound (by ≈0.04 and ≈0.05 eV) isomers with Be relatively far away from the unperturbed respective molecules.

For the 'side' isomer of each complex (Figures 3 and 4), and attachment of Be to one C═C bond makes it stretch by ≈0.4 Å (Table 1), i.e. even more than in Be–C_2H_4, likely due to some release of strain in the ladder-like structure. The binding energy is, accordingly, about twice larger, the Be–C bondlength being same as in Be–C_2H_4.

For the other, 'central' isomer, the Be atom is located on the molecule's symmetry axis (Figures. 3, 4), at the Be–C distances only slightly longer than those in C_2H_4–Be–C_2H_4. However, the insufficient distance between the opposite C═C bonds (imposed by the relatively rigid molecules) does not allow the Be atom to get completely in-between them, more so for the shorter C_6H_6 molecule. This can explain the Be–C_6H_6 binding energy being same as for the corresponding 'side' isomer (Table 1). For the longer C_8H_8 'ladder', with the Be atom pulled further in, the Be–C_8H_8 binding energy is, nevertheless, more than twice that for the 'side' isomer, thus showing some cooperativity. The Be–C_8H_8 binding still, however, remains weaker than for C_2H_4–Be–C_2H_4. Similar 'central'

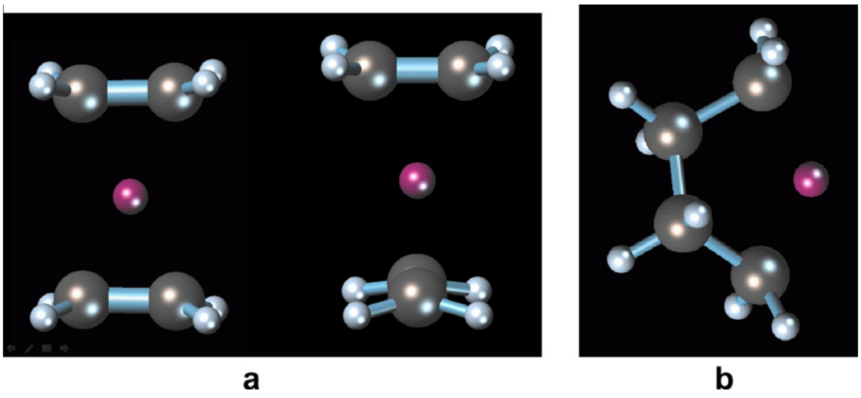

Figure 2. Optimized structures of Be(C_2H_4)$_2$ isomers: C_2H_4–Be–C_2H_4 (a) in the singlet (left) and triplet (right) states, and Be–C_4H_8 (b).

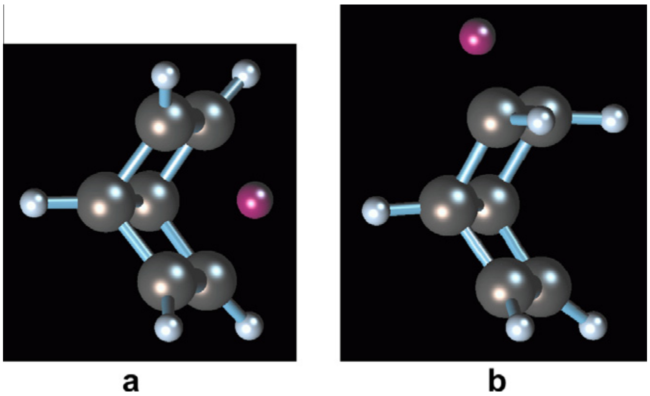

Figure 3. Optimized structures of Be–C_6H_6 'central' (a) and 'side' (b) isomers.

C_8H_8-based isomers have been found previously for cations of Be and Mg atoms, in DFT studies of the possibility of their encapsulation in cubane, resulting in its rupture [22].

Similar to C_2H_4–Be–C_2H_4 as compared to Be–C_2H_4, in spite of stronger binding to the metal atom, the hydrocarbon hosts are distorted, overall, less for the 'central' isomers. The C=C bonds stretch by 0.10 Å only and have lengths very close to those in C_2H_4–Be–C_2H_4. The opposite ends of C_6H_6 and C_8H_8 are pulled slightly closer together by the Be atom (by 0.19 and 0.14 Å, respectively). The triplet-singlet energy gap is much larger for the Be–C_8H_8 system (Table 2). In the triplet state, more rigid Be–C_6H_6 just stretches the Be–C and shrinks the C=C bond similar to C_2H_4–Be–C_2H_4, while the Be–C_8H_8 complex is skewed, with Be shifting to one side and the C=C bonds becoming non-parallel, likely due to part-turning towards perpendicular orientation found for triplet C_2H_4–Be–C_2H_4.

Similar to the above C_2H_4–Be–C_2H_4 → Be–C_4H_8 isomerisation, the 'central' isomer of Be-C_8H_8 can be transformed by converging the C=C units around the Be atom and fusing them together. The resulting 'fused' isomer (Figure 4) is lower in energy than the 'central' one by 0.3 eV only (Table 1), which is much smaller than the 1 eV difference between Be–C_4H_8 and C_2H_4–Be–C_2H_4, as a reflection of rigidity of the C_8H_8 frame strained by this isomerisation. The fusion significantly increases the triplet-singlet energy difference (Table 2). The 'fused' isomer resembles cubane with Be splitting one of its C–C bonds, and removal of Be in this geometry does recover cubane, while requiring ≈3 eV of energy (cubane being less stable isomer of C_8H_8).

By comparison, the 'side' isomers of Mg–C_6H_6 and Mg–C_8H_8 are metastable (Table 1), similar to Mg–C_2H_4. And similar to the above C_2H_4–Mg–C_2H_4 case, the 'central' Mg–C_8H_8 structure is a transition state relaxing into the 'fused' isomer. The latter is slightly metastable to dissociation into Mg + C_8H_8, similar to Mg–C_4H_8, which would suggest a possible efficient catalysis by Mg of the 'ladder' → cubane isomerisation. The triplet-singlet gap is half that for 'fused' Be–C_8H_8 (Table 2), similar to the Mg/Be–C_4H_8 case. The 'central' Mg–C_6H_6 isomer is not found, the corresponding structure relaxing into a weakly bound system (D_e < 0.1 eV).

3.3. M–C_8H_{12}

Another suitable molecule, 1,5-cyclooctadiene C_8H_{12}, a bent cycle with two (non-parallel) C=C bonds on opposite sides, is less strained compared to C_8H_8, its C=C units being structurally closer to those in ethylene in terms of bond angles. In the weakly bound (by ≈0.08 eV) Be–C_8H_{12} system, Be is ≈3.2–3.4 Å away from the nearest C atoms. The Be–C_8H_{12} 'central' isomer (Figure 5) is found to provide same binding energy as for the analogous isomer of Be–C_8H_8 (Table 1), with Be still being not exactly between the C=C bonds. The Be–C_8H_{12} 'side' isomer is, however, much less bound – by about a half relative to Be–C_2H_4 and a third as weakly as for the Be–C_8H_8 'side' isomer. This is likely due to a strain introduced into C_8H_{12} by the attachment, opposite to its release for the C_8H_8 case. Consequently, the gain of stability for Be located between two C=C bonds as compared to being near one such bond is an order of magnitude, effectively resulting in the strongest cooperativity of binding for this case. The triplet-singlet gap for Be–C_8H_{12} is smaller than for Be–C_8H_8 (Table 2).

For the 'central' isomer the Be atom pulls the C=C bonds closer together, similar to the Be–C_8H_8 case, and makes them more aligned. The relevant Be–C and C–C distances in Be–C_8H_{12} are very close to those for the corresponding isomers of Be–C_8H_8 (Table 1), including longer Be–C distances for the 'central' as compared to the

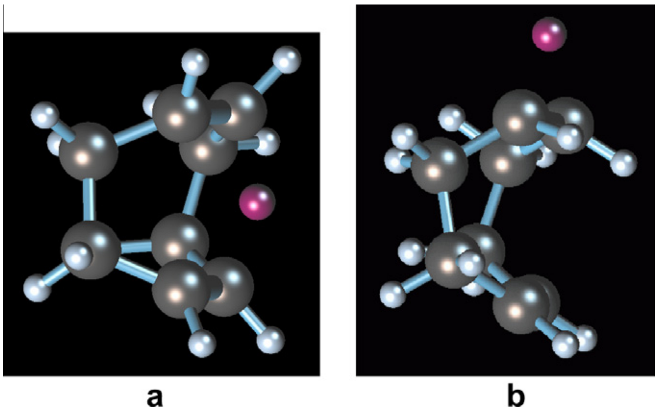

Figure 5. Optimized structures of Be–C_8H_{12} 'central' (a) and 'side' (b) isomers.

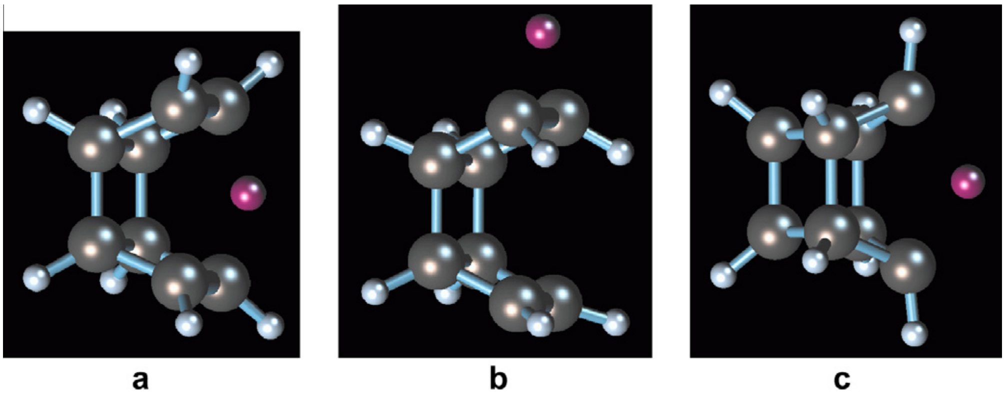

Figure 4. Optimized structures of Be–C_8H_8 'central' (a), 'side' (b), and 'fused' (c) isomers.

'side' isomer. The only appreciable difference is a shorter C–C bond facing Be in the 'side' isomer of Be–C_8H_{12}, whose length is closer to that for Be–C_2H_4. This could again be interpreted in terms of a reduction of strain in the hydrocarbon frame of the 'side' isomer of Be–C_8H_8, consistent with its stronger stabilization.

Similar to the smaller Mg-based counterparts, both 'side' and 'central' isomers of Mg–C_8H_{12} are metastable (Table 1), the energy being lower for the triplet state (Table 2) in accord with the situation for Mg–C_2H_4. For the 'central' isomer, upon attachment of Mg the C–C bond stretches by as much as for 'central' Be–C_8H_{12}, while the system energy increases about as much as it decreases for the Be-based system.

3.4. Properties

Calculated dipole moments of the studied systems show a considerable variation in values (Table 2). The dipoles of the Be complexes (except essentially non-polar C_2H_4–Be–C_2H_4) differ within a factor of 3, from the largest for Be–C_2H_4 to the smallest for the 'fused' isomer of Be–C_8H_8. The 'side' isomers have larger dipole moments relative to those for the 'central' isomers, the values being comparable to that for Be–C_2H_4, indicating mainly local charge transfer. The values for the corresponding Mg complexes are about 3 to 4 times larger, except for Mg–C_2H_4 (2 times).

Positive charges on the metal atoms vary relatively weakly, remaining essentially unchanged within each of two groups: first, C_2H_4–Be–C_2H_4 and all 'central' isomers, and second, Be–C_2H_4 and all 'side' and 'fused' isomers (Table 2). The 2nd group exhibits slightly lower values, qualitatively in accord with smaller number of nearest-neighbour C atoms as electron acceptors. In the Mg-based counterparts, although the ionization energy (IE) of the Mg atom is lower, it is slightly less charged. This suggests the main origin of their larger dipole moments to be longer charge-transfer distances, consistent, in part, with longer metal–carbon separations (Table 1) due to larger size of Mg compared to Be. Another, related contribution comes from the longer projections of the Mg–C bond-dipoles due to smaller C–Mg–C angles.

The closed-shell hydrocarbons and Be (Mg) atom have negative electron affinities, which remains valid for many systems studied here (Table 2), at least for the vertical values (at the geometry of the neutral species). Among the Be complexes, the exceptions (all with low and close VEA values) are Be–C_2H_4 and 'side' isomers of Be–C_6H_6, Be–C_8H_8, and Be–C_8H_{12}, consistent with their larger dipoles, as well as 'fused' Be–C_8H_8. The more polar Mg analogs exhibit larger values, in particular a nonzero VEA for Mg–C_4H_8.

Vertical ionization energies of the Be complexes (Table 2) are generally lower than those of the corresponding isolated hydrocarbons and Be atom (10.5 eV for C_2H_4 and 9–9.5 eV for all other species [21]), with exception of BeC_4H_8. The 'central' isomers of Be–C_6H_6, Be–C_8H_8 and Be–C_8H_{12} show a larger reduction (by 2–3 eV) and have values close to one another and just under that of C_2H_4–Be–C_2H_4, while values for their 'side' isomers and 'fused' Be–C_8H_8 are close to that of Be–C_2H_4. Lower VIE values for the Mg counterparts are in accord with the lower IE value of the Mg atom.

4. Conclusions

Ab initio calculations have been carried out for a series of systems consisting of light Group II metal atoms (Be, Mg) attached to unsaturated hydrocarbon molecules with pairs of double bonds. The case of the atoms sandwiched between two small molecules (C_2H_4) with one double bond is considered as well. In particular, the latter case for Be represents an interesting 'spin switch' system with geometry reversibly altering upon de/excitation.

The metal atom can bind to the molecule weakly (non-covalently) or via attaching to the C=C units, which can also be expected to occur for a huge variety of other molecules with similar structural units. A strong intramolecular cooperativity of binding, with the dissociation energy increasing non-additively (by up to an order of magnitude), can occur for the metal atom located between two aligned double carbon–carbon bonds of the same molecule. Counter-intuitively, these more strongly bound systems show weaker distortion of the molecular components, probably due to resonant switching of metal-atom bonding to two equivalent C=C units, or due to electrostatic repulsion of these (charged and polarized) units. The resonance would be consistent with the charge-transfer from the metal atom being about same for the cases of one and two such units involved.

The binding is sensitive to the position of the metal atom relative to the mid-point between the C=C bonds, as well as to the size of the metal atom. The system with two separate molecules can allow a perfect planar arrangement, with the strong cooperativity of binding (e.g., 7-fold increase for C_2H_4–Be–C_2H_4). The farther the metal atom from the mid-point (as for Be–C_6H_6), in particular due to the larger size of metal atom (e.g., Mg vs Be), the lower the stability, up to metastability (as for Mg systems). Possible alteration of strain in the hydrocarbon component upon metal-atom attachment is another important factor (as for Be–C_8H_{12}).

The C=C units facing the metal atom exhibit π-bond breaking, which facilitates formation of a new C–C bond between two such units converging around the atom. The attached metal atom can thus effectively catalyze the isomerisation of the host molecule (or molecule pair) from unsaturated to saturated, while remaining bound to the product in a stable (as for Be) or metastable way (as for Mg) depending on the atom size.

Systems with low electron affinities and high excitation and ionization energies can be expected to be chemically stable and observable under experimental conditions. This should be especially valid for species which also have high dissociation energies, such as Be$(C_2H_4)_2$, Be–C_8H_8 and Be–C_8H_{12}. To the best of the author's knowledge, such complexes have not yet been studied experimentally, and their predicted unique properties will, hopefully, attract attention now. Such systems could perhaps be produced via reactions of laser-ablated metal with proper hydrocarbons, likely in cryogenic matrices (similar to the cases of smaller molecules). The predicted vertical energies are to facilitate identification of the species, e.g., via photoionization.

Such and similar species (with analogous structural units) may be used in designing stable metal–organic molecular interfaces and metal–atom mediated molecular junctions usable for building larger metal–organic frameworks. Future work will address other analogous systems, including ionic derivatives. In particular, the above larger VIE and VEA of the 'side' as compared to the 'central' isomers would appear to suggest the cooperativity of binding to be higher in the corresponding cations but lower in the anions.

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