Insertion complexes of an organic molecule trapped in ion-pairs

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A group of novel molecule-insertion complexes M–C_3H_6–X (M–X = alkali-halide, -oxide, -hydroxide) is introduced and studied *ab initio*. Charge distributions indicate essentially neutral molecule trapped between opposite ions significantly bending and polarizing it. The system stabilities for different dissociation channels, and structure perturbations by electronic excitation, ionization, and electron attachment are discussed and interpreted. Features of interest include very large dipole moments, excitation-induced selective reactivity of X with C_3H_6, and high energy-storage capacity.

Introduction

Neutral atoms and atomic ions, when interacting with closed-shell molecules, in most cases form weakly bound complexes due to van der Waals attraction and polarization. Ions interact with one another much more strongly *via* Coulomb forces, normally forming, for opposite charges on ions, highly stable charge-transfer systems such as alkali-metal halides and oxides. Such polar systems interact with closed-shell molecules more weakly than separate ions due to partial cancellation of the electric fields of the oppositely charged ions. The latter is valid for the usual case of the closed-shell molecule being *outside* the ion-pair.

If, however, the molecule was inserted in-between the ions, the electric field acting on it would be increased, and the ions would be bound effectively *via* a charge transfer through the molecule. Stability of such systems depends on how well the inserted molecule is trapped inside the stretched ion-pair which would tend to recombine by squeezing the molecule out. If the recombined ion-pair plus the molecule correspond to a lower energy, then the insertion complexes are metastable. Another factor of stability is preservation of the ion-pair character with stretching, as in many cases the neutral-atom asymptote is lower in energy. In particular, metal-halides have the corresponding switch at rather long distances ($\sim$10 Å), allowing some space for accommodating the molecule.

Previous relevant studies have dealt with inserted either closed-shell (rare-gas) atoms, such as in M′–Rg–X (M′ = noble metal; Rg = Ar, Kr, Xe; X = F, OH) ,[1,2] or unsaturated organic molecules (such as benzene and its derivatives) and then focused on the ion-pi interactions, *e.g.* in M–C_6H_6–X, M–C_6F_6–X, M–$C_3N_3H_3$–X (M = alkali metal, X = halogen).[3–5] Another family of systems, with *no* such interactions because of a saturated molecule is M–$C_2X'_6$–X (X′ = halogen same or different from X) complexes ,[6,7] with M^+ and X^- at the hollows of the CX'_3 groups. By contrast, the M–C_2H_6–X counterparts are unstable, with the ethylene molecule squeezed out and MX recombined due to the CH_3 groups with shorter C–H bonds being unable to hold the ions. In the present work, another structurally analogous molecule, cyclopropane C_3H_6, is investigated, with more space in-between three C–H bonds on each side of the carbon cycle, allowing M and X to sink deeper into the hollows, stabilizing the system. In addition, various X (halogen, oxygen, OH) are considered.

Systems with ion-pairs stretched by trapped molecules can be anticipated to have large dipole moments (*e.g.* up to $\approx$40 D for M–C_2F_6–X),[7] facilitating intense interaction with radiation and suggesting light-sensor and related applications. The metastability may facilitate energy storage at molecular level. Besides, the systems of interest here represent small organic molecules whose structure and related properties (electronic, spectral, *etc.*), modified in the strong electric field of the attached ion-pairs, could be of interest as well.

Computational procedure

In view of intense charge-transfer and non-covalent interactions determining the interactions in the systems, an MP2 (Møller–Plesset 2nd-order perturbation theory) approach is preferred in this work, consistent with the previous studies mentioned above. The aug-cc-pVTZ basis sets for the 1st and 2nd row atoms (H, Li, C, O, F), and Stuttgart's relativistic effective core potentials (ECP) RSC/RLC and associated basis sets for heavier atoms (Cs, I) are used, all detailed in the Basis Set Exchange.[8] Both the method and the ECPs/bases are implemented in the NWChem *ab initio* package employed.[9]

Complete all-atom geometry optimizations in a low (C_1) symmetry are performed for all species. Local energy minima are verified in terms of all-real vibrational frequencies. Higher-spin electronic states are also investigated, and both neutral and ionic systems are considered. Charge distributions over atoms are characterized using natural charges calculated with the NBO (Natural Bond Orbital) code (available, *e.g.*, at http://www.ccl.net/cca/software/MS-WINDOWS/mopac6/index.shtml). Visualization and analysis of the obtained structures and electron density are carried out using the ViewMol3D and Molekel software.[10,11]

Results and discussion

As a first step, the C_3H_6 molecule is pre-optimized at the chosen level of theory. Its calculated total electron density

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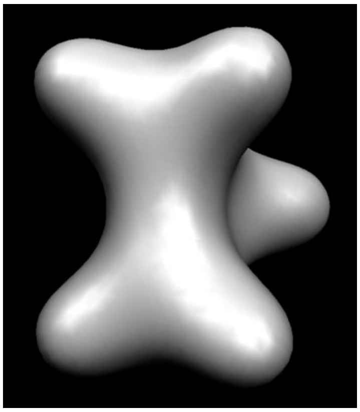

Fig. 1 Calculated ground-state electron density of C_3H_6.

(Fig. 1) exhibits a concave shape with three humps (due to H atoms) on each side of the C_3 cycle, appropriate for holding an atom.

Placing a metal and a halogen atom on the opposite sides of the molecule and relaxing the energy leads to a system with a typical geometry of near-C_{3v} symmetry, shown in Fig. 2, with the added atoms remaining in the axis of C_3H_6. The molecule is visibly bent, with the hydrogen atoms slightly converging to the halogen atom and slightly diverging from the metal atom. This is consistent with the anticipated charges of the framing atoms (positive M and negative X) and their Coulomb interactions with positive H atoms.

The geometry parameters for the four metal-halogen combinations studied (M = Li, Cs and X = F, I) are collected in Table 1. The molecule is slightly perturbed, with the C–C bonds and the C–H bonds stretched within $\approx$0.01 Å relative to respective 1.50 Å and 1.08 Å in the isolated C_3H_6, and the HCC angles deviating within $\approx 8^\circ$ from 118° in the isolated molecule and being up to $\approx 14^\circ$ larger on the side of metal. The M–X separation increases with the size of either M or X, remaining within 7 Å for all cases and thus ensuring the ion-pair character of the M–X frame and hence stability of the system. The equilibrium distances R_e(M–C) and R_e(C–X) vary similarly. For a given M the R_e(M–C) values increase only marginally (by $\approx$0.02 Å) from X = F to I, while for a given X the R_e(C–X) distances stretch more noticeably (by $\approx 0.07 \pm 0.01$ Å) from M = Li to Cs.

Table 1 Equilibrium parameters (in eV, Å, degree) of the M–C_3H_6–X complexes

System	D_e	R_e(M–C)	R_e(C–X)[a]	R_e(M–X)	∠HCC[b]
Li–C_3H_6–F	3.37	2.06	2.63	4.35	123/111
Li–C_3H_6–F^-	1.15	2.25	2.79	4.73	121/113
Li–C_3H_6–F^+	0.77	2.23	2 × 3.30, 3.38	5.26	122/117
Li–C_3H_6–I	2.32	2.08	3.27	5.04	124/110
Li–C_3H_6–I^-	1.38	2.27	3.37	5.36	122/112
Li–C_3H_6–I^+	1.25	2.16–2.19	2 × 3.49, 3.58	5.41	123/115
Cs–C_3H_6–F	3.86	3.14	2.71	5.58	121/112
Cs–C_3H_6–F^-	1.25	3.30	2.82	5.87	120/113
Cs–C_3H_6–I	2.91	3.16	3.33	6.25	122/112
Cs–C_3H_6–I^-	1.50	3.33	3.40	6.50	120/113
Cs–C_3H_6–I^+	0.77	3.39	3.24, 2 × 3.51	6.55	120/116
Li–C_3H_6–O	0.98	2.06–2.08	2 × 2.61, 2.85	4.40	123/112
Li–C_3H_6–O^-	1.62	2.02	2.59	4.26	124/103
Li–C_3H_6–O^+	0.80	2.22	3.40	5.33	122/117
Li–C_3H_6–OH	1.87	2.06	2.66–2.68[c]	4.39[d]	123/111
Li–C_3H_6–OH^-	1.18	2.25	2.84[c]	4.78[d]	121/113
Li–C_3H_6–OH^+	1.01	2.20	3.17[c]	5.07[d]	122/117

[a] Notations of the form "2 × L" mean 2 bonds of length L. [b] on M/X side. [c] C–O distance. [d] Li–O distance.

The M–C_3H_6–X → M + C_3H_6 + X dissociation energies (Table 1) decrease by $\approx$1 eV from X = F to I (for either M) and increase by $\approx$0.5 eV from M = Li to Cs (for either X). These variations can be qualitatively explained in terms of relative electronegativities of the framing atoms. The lower the ionization energy (IE) of M and/or the higher the electron affinity (EA) of X, the stronger the M–X charge-transfer and the higher the stability of the system. The previously studied M–C_2F_6–X systems have exhibited similar trends ,[7] the D_e values being smaller (twice for MX = CsI) due to longer R_e(M–X).

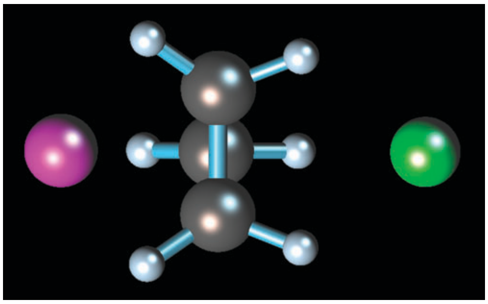

Fig. 2 Optimized geometry of the ground state Li–C_3H_6–F.

Indeed, the charge on M increases slightly (by $\approx$0.05 e) from Li to Cs and the charge on X decreases (in absolute value) more appreciably (by $\approx$0.1 e) from F to I (Table 2), even quantitatively in accord with the above variations in D_e. All, up to minor, variations in the charge values correlate to the relative values of IE(M) and EA(X). The metal atoms in the systems are essentially full cations, while the halogen atoms are anionic to a lesser degree, especially iodine. The molecule is then slightly negatively charged within the complex

Table 2 Atomic charges (in e), dipole moments (D), electron affinities and ionization energies (eV) of the M–C_3H_6–X complexes

System	q(M)	q(X)	μ/EA/IE
Li–C_3H_6–F	0.96	−0.91	14.5[a]
Li–C_3H_6–F^-	0.06	−0.94	1.43[b]
Li–C_3H_6–F^+	0.98	0.01	7.95[c]
Li–C_3H_6–I	0.96	−0.77	16.6[a]
Li–C_3H_6–I^-	0.06	−0.87	1.67[b]
Li–C_3H_6–I^+	0.98	0.06	6.42[c]
Cs–C_3H_6–F	1.01	−0.93	21.2[a]
Cs–C_3H_6–F^-	0.09	−0.95	1.03[b]
Cs–C_3H_6–I	1.01	−0.84	23.9[a]
Cs–C_3H_6–I^-	0.08	−0.89	1.19[b]
Cs–C_3H_6–I^+	1.01	0.03	5.67[c]
Li–C_3H_6–O	0.96	−0.88	14.7[a]
Li–C_3H_6–O^-	0.87	−1.62	2.07[b]
Li–C_3H_6–O^+	0.98	0.01	5.52[c]
Li–C_3H_6–OH	0.97	−0.91 (−1.35)[d]	13.3[a]
Li–C_3H_6–OH^-	0.06	−0.95 (−1.37)[d]	1.38[b]
Li–C_3H_6–OH^+	0.98	0.01 (−0.44)[d]	6.20[c]

[a] μ (D). [b] EA (eV) of neutral species. [c] IE (eV) of neutral species. [d] q(O).

by −q(X) −q(M) ≈ −0.05 e (in Li–C_3H_6–F) to ≈ −0.2 e (in Li–C_3H_6–I), consistent with its polarization by the field of the ions (reflected in its induced asymmetry along the axis, discussed above). This is similar to the charge distributions in M–C_2F_6–X,[7] but different from a considerable positive charge on Rg (hence reduced charge on M′) in M′–Rg–F[1,2] and from slightly positive molecule in Na–C_6H_6–X.[3]

Comparison with the analogous π-bonded systems M–C_6H_6–X[4] shows a similar decrease of their D_e values for heavier X (for a given M), while an opposite decrease of D_e also for heavier M (for a given X). In addition, Li–C_6H_6–X are considerably (up to twice for heavier X) more stable to dissociation than corresponding Li–C_3H_6–X, which difference is diminished or perhaps even reversed for heavier M. The M–C_6F_6–X counterparts have exhibited similar variations,[4] hence in part different from those for M–C_2F_6–X.[7]

The above results suggest the following qualitative interpretation of the (mainly electrostatic) nature of interactions in the systems studied. The framing ions of opposite charges are attracted to one another by Coulomb interactions and trap the (appropriately concave) molecule between them *via* a combination of mechanical (steric) hold, relatively weak charge-transfer (to the molecule), and polarization. This can be confirmed in the following approximate fragmentation of the total interaction. Dissociation energies (relative to the same limit of separate M, C_3H_6, X) are calculated, at the same level of theory, for the M^+–C_3H_6, C_3H_6–X^- and M–X fragments frozen in their geometries inside optimized M–C_3H_6–X. These energies are dominated by the M–X component (except for MX = LiI) and add up to 2.44, 1.59, 3.23, 2.33 eV for, respectively, MX = LiF, LiI, CsF, CsI, or ≈70-80% of the total D_e values (*cf.* Table 1). The remaining interaction energy can be attributed to (non-additive) three-body interactions including, *e.g.*, energies of the dipoles on C_3H_6 induced by one framing ion, in the field of the other one.

Dipole moments of the M–C_3H_6–X systems vary, by definition, in accord with the charge transferred between M and X as well as the (M–X) distance of this transfer. The dipoles increase significantly (by ≈50%) from M = Li to Cs for a given X and slightly (by ≈10%) from F to I for a given M, the overall variation of their values matching that of R_e(M–X). The charge-transfer distance thus appears to be a dominating factor. The dipole moment values exceed those of respective MX diatoms by a factor of ≈1.5 (for MX = CsF) to ≈2.5 (LiF) due to far-separated ions, but are less than for M–C_2F_6–X [7] because of shorter R_e(M–X).

All the systems have closed-shell ground states. Excitation to a triplet state destabilizes the system due to reducing the MX ion-pair to two non-bound neutral atoms, with M flying away. This is consistent with the analogous situation for the isolated MX diatom. Unlike for the X = I case, upon such an excitation the chemically more active neutral F atom appears to react with C_3H_6 (for both M = Li and Cs), forming HF (Fig. 3). The vertical excitation (at the frozen ground-state geometry) exhibits moderate (≈2.4–2.5 eV) and high (≈6.2–6.3 eV) energies VE* for the species with X = I and F, respectively. This is consistent with stronger H–F hydrogen bonds being lost upon the excitation (hence neutralization of X).

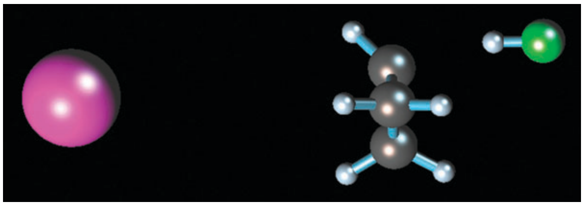

Fig. 3 Optimized geometry of Cs–C_3H_6–F for the (excited) triplet state.

Electron attachment to M–C_3H_6–X is essentially localized (by 90% in terms of charge) on M^+, thus almost neutralizing the metal ion (Table 2). As a result, both framing atoms somewhat withdraw from the molecule, more so the M atom (Table 1). In accord with a lower stability of isolated MX^- relative to MX, the D_e value of M–C_3H_6–X^- is decreased relative to the neutral system, by about two thirds for X = F to about half for X = I. The weaker interaction of the framing atoms with the molecule is reflected in its somewhat smaller bending. Accordingly, the electron affinities of M–C_3H_6–X are moderate, under 2 eV, with relative values correlating to the ionization potentials of M for a given X and to the dipole moments of neutral species for a given M (Table 2). The corresponding vertical electron affinities (at the frozen geometries of neutral species) are same as adiabatic ones within ≈0.1 eV.

Ionization of M–C_3H_6–X essentially removes electron from X^-, thus making the halogen atom almost neutral (Table 2). This also stretches the system, with both R_e(M–C) and, mainly, R_e(C–X) increasing (Table 1). Accordingly, the binding energy drops even more for the cationic systems as compared to the anions (up to breaking Cs–C_3H_6–F^+, with Cs departing), likely due to the loss of considerable hydrogen bonding between H's and X^-. While in M–C_3H_6–X^- the framing atoms remain in the molecular axis, the halogen atom slightly shifts away from it in M–C_3H_6–X^+. The molecule is bent even less in the cationic as compared to the anionic system, the difference between the HCC angles on the metal and halogen sides being smaller. The ionization energies are rather low (Table 2) and vary in accord with the electron affinities of X for a given M and with the inverse of the M–X distance (hence Coulomb attraction of electron to M^+) for a given X.

The energy of M–C_3H_6–X relative to MX + C_3H_6 describes stability of the system for such a dissociation channel and is given by D_e(MX)–D_e(M–C_3H_6–X). These values decrease quickly from X = F to I for a given M and from M = Li to Cs for a given X (2.87, 1.61, 1.37, −0.21 eV for MX = LiF, LiI, CsF, CsI). The values are positive for all above species except Cs–C_3H_6–I, indicating their metastability, with a potential barrier towards the dissociation. Hence there is a similarity to metastable M′–Rg–F, M–C_6H_6–X, M–C_6F_6–X and M–C_2F_6–X species ,[1–4,7] with exception of (also metastable) Cs–C_2F_6–I. The energy barriers for C_3H_6 release from in-between M and X are evaluated to be rather low (under 0.1 eV), reflecting the short C–H bonds in C_3H_6 (holding the framing atoms) and increasing from M = Li to Cs and (more quickly) from X = F to I. Unlike for the heavier systems, for

MX = LiF the related shift of C_3H_6 is followed by reaction with F, forming HF.

Another meaning of the above difference in D_e is how much energy could be stored in the system and released *via* its dissociation followed by recombination of the metal halide diatom. The negative value for Cs–C_3H_6–I indicates some stability of this system to such dissociation, and can be related to the shallowest potential energy curve of CsI among MX studied here. Indeed, with the MX diatom stretching to the M–X distance in M–C_3H_6–X, its calculated binding energy is reduced most for MX = LiF (by ≈4.5 eV) and least for MX = CsI (by ≈1.3 eV). Insertion of the C_3H_6 molecule in-between M^+ and X^- results in its (mainly electrostatic) interaction with the ions, compensating the loss of binding (caused by the M–X stretch) in part or, for MX = CsI, more than in full. By comparison, for Cs–C_2F_6–I the Cs–I stretch, hence the loss of binding, is larger.[7]

Replacing F in Li–C_3H_6–F by O results in a similar complex, with the Li–C distances being almost same, but with the O atom shifted slightly away from the molecular axis (Table 1). The system is, however, much less stable (more than threefold) to dissociation, in accord with the relation between LiF and LiO exhibiting the same difference (≈2.4 eV) in the D_e values.[12] This could be related to a lower electronegativity of oxygen relative to fluorine as well as the open-shell character of Li–C_3H_6–O. Nevertheless, the charges on Li and O as well as the Li–O distance in Li–C_3H_6–O are very close to those for the X = F case, leading to nearly same dipole moment (Table 2).

Excitation of Li–C_3H_6–O to the higher-spin (S = 3/2) state leads to dissociation of the system, with Li flying away. Electron attachment makes the molecule negative by about twice as much (≈ −0.25 e) as in Li–C_3H_6–F^-, while, unlike for the X = F case, adds most of extra electron density to the (divalent) O atom, making it a nearly doubly charged ion (Table 2). This result in a slight compression along the axis, recovery of axial alignment (with all R_e(C–O) being same), slightly longer C–C bonds (stretched by ≈0.02 Å) and larger bending of the molecule due to stronger H–O Coulomb interactions, with the HCC angles on the O side being ≈20° smaller than on the Li side (Table 1). Another consequence is a higher stability of the anionic as compared to the neutral complex, opposite to the X = F case. Moreover, since the extra electron goes to oxygen, the electron affinity of Li–C_3H_6–O is higher than for Li–C_3H_6–F (Table 2). Ionization removes electron density from O, resulting in a withdrawal of Li and (more significantly) O from the molecule, even quantitatively close to the X = F case. Due to lower EA of O relative to F, the ionization energy is lower for the X = O case.

Finally, a Li–C_3H_6–OH complex is considered, with the molecular (diatomic) X species, which also forms a stable system with OH lying in the molecular axis and pointing with its H-end away from the molecule (Fig. 4) due to repulsion from H′s in C_3H_6, unlike, *e.g.*, in Au–Rg–OH (with OH at an angle).[2] This closed-shell species has a higher D_e than Li–C_3H_6–O, at more than half the value for Li–C_3H_6–F (Table 1). The charges on Li and OH are nearly same as for X = O and X = F (Table 2), the dipole moment being 10% smaller because of the contribution of opposite sign due to positive H (at ≈ + 0.4 e). The system is higher in energy relative to LiOH + C_3H_6 by 2.99 eV, close to the value for X = F, with the potential barrier for releasing the trapped molecule of ≈0.03 eV.

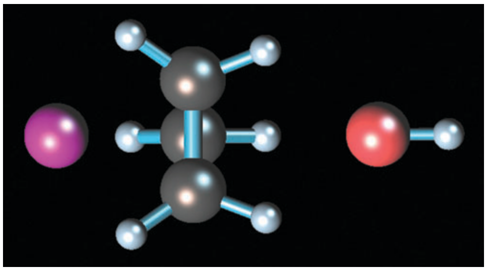

Fig. 4 Optimized geometry of the ground state Li–C_3H_6–OH.

The isoelectronic Li–C_3H_6–OH system behaves very similar to Li–C_3H_6–F upon electron-attachment and ionization, except for the latter process the electron density being removed only from the O atom of OH. The resulting ionic derivatives are, however, slightly more stable to dissociation than those for X = F, especially the cation (Table 1). For the anion, the presence of H in OH thus alters the system parameters (charges, D_e) relative to Li–C_3H_6–O considerably. Consistent with the extra electron going to Li^+, the electron affinity of Li–C_3H_6–OH is close to that for Li–C_3H_6–F (Table 2). The ionization energy of Li–C_3H_6–OH is between those for Li–C_3H_6–O and Li–C_3H_6–F, in accord with the relative EA values of X = OH, O, F.[12] While VE* ≈ 2.5 eV of Li–C_3H_6–OH is same as for X = F, excitation to the triplet state does not make less reactive X = OH to react with C_3H_6.

Conclusions

A series of charge-transfer complexes M–C_3H_6–X with a small organic molecule trapped between two counter-ions (of M = alkali metal and X = halogen/oxygen/hydroxyl) is investigated computationally at an MP2 level of theory. The systems are dominated by electrostatic interactions (including polarization) and are metastable relative to the recombined ion-pair plus molecule for all cases except Cs–C_3H_6–I which appears to be somewhat bound. Such a metastability could enable energy storage at molecular level, with up to ≈3 eV per complex. The potential barriers for removal of the trapped molecule from in-between the ions are low, implying the system stability only under low-temperature conditions, while enabling a relatively easy release of the stored energy *via* moderate heating. The stability is expected to be higher for the M–C_3F_6–X counterparts, based on the metastability of analogous M–C_2F_6–X *versus* instability of M–C_2H_6–X.[7]

The considered species are representatives of a large class of similar systems based on a huge variety of organic molecules with appropriate cyclic units to which various ion-pairs (both atomic and molecular) could be attached. In the electric field of the framing ions, the molecule is significantly polarized and perturbed structurally, while remaining essentially neutral. Such ion-pair attachments could thus change reactivity of the organic molecular "hosts" as well as their long-range interactions due to large dipole moments (up to $\approx$24 D for the studied cases).

Most of the systems are found to survive ionization and electron attachments, while altering their geometry, mainly *via* stretching along the axis due to neutralization of one of the framing ions (except for the Li–C_3H_6–O^- case), more significantly for the cationic derivatives. The neutral species are closed-shell (except for the $X = O$ case) and are destroyed by electronic excitation (to the triplet state) causing dissociation or a reaction of $X = F$ with the molecule, forming HF.

The systems could be produced experimentally, *e.g. via* photodissociation of ion-pair MX diatoms in $(C_3H_6)_n$ clusters, followed by recombination of recoiling M and X, with C_3H_6 likely to be in the way. The mechanism may thus be similar to that proposed for formation of H–Rg–X species in the rare gas (Rg) solids[13] and can be anticipated to be more efficient than, *e.g.*, for formation of M–$C_2X'_6$–X species,[7] due to C_3H_6 being more oblate in shape and having larger area in the proper direction. Besides, the H–Rg–X species have been readily produced *via* photodissociation of HX in rare gas clusters.[14]

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