Introduction

The activation of H₂ molecule by frustrated Lewis pairs (FLPs) has attracted much attention over the past years. 1–6 Group 13–15 compounds, in particular, B-P FLP are very active in heterolytic hydrogen splitting. 7 Nitrogen-containing FLP are less common. 4–6 Nature of the Lewis acid is expected to play a significant role in energetics of the hydrogen splitting. Fluorination of group 13 element ary derivatives significantly reduces standard enthalpies of the heterolytic hydrogen splitting H₂ + D + A → [HD]⁺ + [HA]⁻. Analysis of several types of the [HD]⁺…[HA]⁻ ion pair formation in the gas phase reveals that structures with additional H—F interactions are energetically favorable. Taking into account the ion pair formation, hydrogen splitting is predicted to be highly exothermic in case of the fluorinated derivatives both in the gas phase and in solution. Thus, fluorinated adamantane-based Lewis superacids are attractive synthetic targets for the construction of the donor–acceptor cryptands. © 2016 Wiley Periodicals, Inc.

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1-Boraadamantane and its complexes with N-containing donors are known laboratory species. In addition, Bubnov et al. reported that reaction of 1-boraadamantane with 1-azaadamantane results in a DA complex (Scheme 1), which is stable toward atmospheric air and moisture. Synthesis of perfluorinated adamantane derivatives also seems viable due to success of the direct low temperature fluorination. Thus, 1-boraadamantane and its fully fluorinated derivatives emerge as viable building blocks for the construction of DA cryptands with pyramidalized group 13 environment. Analysis of the thermodynamics of the hydrogen splitting process is crucial for the correct choice of the Lewis acid-base combination.

In order to provide the best combination of donor and acceptor fragments for the construction of hydrogen splitting cryptands, in the present work we have undertaken a detailed computational study of donor–acceptor complexes formed by group 13 element adamantane and fully fluorinated adamantane derivatives EC9R15 with nitrogen and phosphorus-containing Lewis bases XR3 and XC9H15 (E = B, Al; R0 = H, F; X = N, P; R = H, CH3) using the generalized gradient approximation (GGA) of density functional theory (DFT) in the form of BP86 functional with all electron TZ2P basis set.

We present a consistent set of structural data for the studied complexes and report thermodynamic characteristics for their

![Scheme 1. Structure of 1-azaadamantane 1-boraadamantane complex.](image)

![Figure 1. Optimized structures of donor–acceptor complexes: a) XR3 EC9R15; b) XC9H15 EC9R15 (X = N, P; E = B, Al; R = H, CH3; R0 = H, F).](image)
formation and reactions with molecular hydrogen. Results of energy decomposition analyses (EDA) and molecular orbital (MO) features of donor–acceptor complexes are presented. Finally, the influence of the donor and acceptor fragments on the thermodynamics of the heterolytic hydrogen splitting is also discussed. Obtained results can serve as a guideline for the construction of the DA cryptands for the heterolytic hydrogen splitting process.

**Computational Details**

**General procedures**

DFT calculations were performed with the Amsterdam Density Functional (ADF) program. The molecular orbitals (MOs) were expanded in a large uncontracted set of Slater type orbitals (STOs) of triple-$\zeta$ quality for all atoms including two sets of polarization functions. An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular density and to represent the quality for all atoms including two sets of polarization functions. An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular density and to represent the Coulomb and exchange potentials accurately for each SCF cycle. Energies and gradients were computed using the local density approximation (Slater exchange and VWN correlation) with non-local corrections for exchange (Becke88) and correlation (Perdew86) included self-consistently (i.e., BP86 functional). Analytical Hessians were computed to confirm that optimized geometries correspond to the true minima on the respective potential energy surfaces (PES). Standard enthalpies, entropies, and Gibbs energies were calculated from frequency computations using classical statistical-mechanics relationships for an ideal gas. Solvent effects in toluene solution are treated with the COSMO model, which takes into account the cavitation and dispersion contributions to the solvation free energy. BP86/TZ2P level of theory yields a mean absolute deviation (MAD) for proton affinities (at 298 K) of several neutral bases across the periodic table of 1.9 kcal mol$^{-1}$ with respect to experiment. For the best combination of Lewis acid BC$_{9}$F$_{15}$ and Lewis base NC$_{9}$H$_{15}$ we have compared standard enthalpies of the gas phase heterogeneous hydrogen splitting with formation of the isolated ions (process (4), vide infra). Values at BP86/TZ2P, M06-2X/6-311G**, and B3LYP/TZVP levels of theory are 4.27, 5.33, and $-1.33$ kcal mol$^{-1}$, respectively. Thus, values at BP86/TZ2P level are within 1 kcal mol$^{-1}$ of M06-2X/6-311G** results and by 5 kcal mol$^{-1}$ less exothermic than B3LYP/TZVP results. Thus, our qualitative conclusions about the energetic favorability of the reactions are expected to be correct.

**Bond energy decomposition analysis**

An energy decomposition analysis (EDA) has been carried out considering the process D + A $\rightarrow$ DA that corresponds to the interaction of donor (D) fragment with acceptor (A) fragment. The complex formation energy ($\Delta E$) can be written as a sum of two components [eq. (1)]:

$$\Delta E = \Delta E_{\text{def}} + \Delta E_{\text{int}}$$

In this formula, the deformation energy $\Delta E_{\text{def}}$ is the amount of energy required to deform the separated donor and acceptor fragments from their equilibrium structures to the geometry that they acquire in the complex. The interaction energy $\Delta E_{\text{int}}$ corresponds to the energy change when the prepared (deformed) fragments are combined to form DA complex. It is analyzed in the framework of the Kohn-Sham MO model using a Morokuma-type decomposition of the interaction energy into electrostatic interaction, exchange (or Pauli) repulsion, and orbital interaction terms [eq. (2)].

$$\Delta E_{\text{int}} = \Delta V_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{ox}}$$

The term $\Delta V_{\text{elstat}}$ is usually attractive. It corresponds to the classical electrostatic interaction between the unperturbed charge distribution of the prepared (deformed) fragments. The Pauli repulsion $\Delta E_{\text{Pauli}}$ comprises the four-electron destabilizing interactions between occupied MOs. The orbital interaction $\Delta E_{\text{ox}}$ term accounts for the charge transfer (i.e., donor–acceptor interactions between occupied orbitals on one fragment with unoccupied orbitals of the other, including the HOMO–LUMO interactions) and polarization (empty–occupied orbital mixing on one fragment due to the presence of another fragment).

**Results and Discussion**

**Structural and energetic features of the donor–acceptor complexes**

The optimized geometries of the closed-shell singlet ground state of donor–acceptor complexes are shown in Figure 1. All complexes are $C_{3v}$ symmetric. Table 1 summarizes selected geometric parameters of the compounds. The

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**Table 1. Selected geometrical parameters of studied complexes (bond lengths d and r in Å and angles $\alpha$ in degrees).**

| Compound | d (X-E) | r(E-C) | $\alpha$ (C-E-C) | $\Delta E^d_{H298}$ | $\Delta S^d_{H298}$ | $\mu$ (in Debye) |
|----------|---------|--------|-----------------|---------------------|-------------------|-----------------|
| NH$_3$:BC$_9$H$_{15}$ | 1.657 | 1.625 | 110.3 | 17.9 | 37.4 | 5.08 |
| NH$_3$:BC$_9$F$_{15}$ | 1.591 | 1.628 | 108.7 | 63.0 | 38.2 | 8.07 |
| NC$_9$H$_{15}$:BC$_9$H$_{15}$ | 1.732 | 1.635 | 109.2 | 16.3 | 47.6 | 5.07 |
| NC$_9$H$_{15}$:BC$_9$F$_{15}$ | 1.653 | 1.660 | 105.9 | 57.1 | 52.2 | 9.39 |
| NC$_9$H$_{15}$:BC$_9$F$_{15}$ | 1.722 | 1.638 | 108.9 | 19.1 | 47.5 | 6.02 |
| PH$_3$:BC$_9$H$_{15}$ | 1.992 | 1.633 | 110.8 | 8.6 | 44.7 | 3.49 |
| PH$_3$:BC$_9$F$_{15}$ | 1.955 | 1.635 | 108.9 | 48.6 | 41.1 | 8.37 |
| PH$_3$:BC$_9$F$_{15}$ | 1.973 | 1.643 | 109.5 | 20.2 | 44.0 | 5.51 |
| PH$_3$:BC$_9$F$_{15}$ | 1.980 | 1.644 | 107.4 | 68.3 | 43.5 | 10.70 |
| PH$_3$:BC$_9$F$_{15}$ | 1.975 | 1.643 | 109.5 | 20.8 | 54.1 | 6.27 |
| PH$_3$:BC$_9$F$_{15}$ | 1.974 | 1.642 | 107.5 | 69.0 | 49.0 | 12.39 |
| NH$_3$:AI$_{9}$CH$_{3}$ | 2.087 | 1.985 | 106.7 | 23.2 | 32.1 | 6.34 |
| NH$_3$:AI$_{9}$CH$_{3}$ | 2.002 | 2.018 | 101.9 | 48.5 | 34.0 | 12.09 |
| NH$_3$:AI$_{9}$CH$_{3}$ | 2.084 | 1.991 | 106.0 | 25.2 | 41.6 | 6.38 |
| NH$_3$:AI$_{9}$CH$_{3}$ | 1.977 | 2.027 | 100.9 | 53.3 | 37.1 | 13.05 |
| NH$_3$:AI$_{9}$CH$_{3}$ | 2.065 | 1.993 | 105.7 | 29.4 | 52.9 | 7.67 |
| NH$_3$:AI$_{9}$CH$_{3}$ | 1.959 | 2.029 | 100.5 | 51.9 | 43.2 | 15.10 |
| PH$_3$:AI$_{9}$CH$_{3}$ | 2.587 | 1.984 | 107.2 | 11.9 | 28.4 | 4.84 |
| PH$_3$:AI$_{9}$CH$_{3}$ | 2.471 | 2.026 | 101.9 | 34.0 | 45.5 | 12.37 |
| PH$_3$:AI$_{9}$CH$_{3}$ | 2.517 | 1.995 | 105.7 | 22.8 | 50.3 | 7.36 |
| PH$_3$:AI$_{9}$CH$_{3}$ | 2.424 | 2.033 | 100.5 | 52.8 | 46.8 | 15.30 |
| PH$_3$:AI$_{9}$CH$_{3}$ | 2.517 | 1.995 | 105.5 | 22.9 | 51.6 | 8.45 |
| PH$_3$:AI$_{9}$CH$_{3}$ | 2.419 | 2.034 | 100.2 | 54.3 | 53.0 | 17.52 |
Table 2. Results of energy decomposition analysis (all values in kcal mol\(^{-1}\)) for boron-containing complexes.

| NH\(_2\)BC\(_{11}\)H\(_{15}\) | NH\(_2\)BC\(_{11}\)F\(_{15}\) | \(\Delta E\)\[^{[a]}\] |
|-----------------|-----------------|-------------|
| \(\Delta E_{\text{F,elect}}\) | 140.91 | 140.91 |
| \(\Delta E_{\text{static}}\) | -92.47 | -117.62 |
| \(\Delta E_{\text{disp}}\) | -92.47 | -117.62 |
| \(\Delta E_{\text{int}}\) | -59.82 | -59.82 |
| \(\Delta E\) | -18.60 | -18.60 |

**Table 3. Results of energy decomposition analysis (all values in kcal mol\(^{-1}\)) for aluminum-containing complexes.**

| NH\(_3\)AlC\(_{11}\)H\(_{15}\) | NH\(_3\)AlC\(_{11}\)F\(_{15}\) | \(\Delta E\)\[^{[a]}\] |
|-----------------|-----------------|-------------|
| \(\Delta E_{\text{F,elect}}\) | 64.50 | 64.50 |
| \(\Delta E_{\text{static}}\) | -61.70 | -61.70 |
| \(\Delta E_{\text{disp}}\) | -29.87 | -29.87 |
| \(\Delta E_{\text{int}}\) | -27.07 | -27.07 |
| \(\Delta E\) | -28.74 | -28.74 |

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Cartesian coordinates of all studied complexes are provided in the Supporting Information (Table S1).

Thermodynamic parameters (standard dissociation enthalpies and entropies) are also given in Table 1, together with dipole moments. As can be seen from Table 1, dissociation enthalpies of complexes with BC\(_{11}\)H\(_{15}\) are in the range 8.6–20.8 kcal mol\(^{-1}\). These values can be compared with experimental gas phase dissociation enthalpies of 1-Quinuclidine-BMe\(_3\) and 1-pyridine-1-boraadamantane complexes (19.9 ± 1 kcal mol\(^{-1}\) and 22.7 ± 0.7 kcal mol\(^{-1}\), respectively). The fluorination of the acceptor moiety does not affect much the standard dissociation entropies, which are in range 28–54 cal mol\(^{-1}\) K\(^{-1}\) for the non fluorinated and 34–55 cal mol\(^{-1}\) K\(^{-1}\) for fluorinated compounds. Computed dipole moments of 1-boraadamantane complexes (Table 1) are comparable with experimental values of dipole moments in benzene solution for 1-boraadamantane-pyridine (6.0 ± 0.15 D) and 1-boraadamantane-quinuclidine (6.2 ± 0.2 D). The fluorination of the acceptor moiety dramatically increases the dissociation enthalpy of the boron-containing complexes (by about 40–48 kcal mol\(^{-1}\)). For aluminum-containing compounds fluorination effect is smaller than for boron analogues (dissociation enthalpies increase by about 22–31 kcal mol\(^{-1}\)). Note that complexes with BC\(_{11}\)F\(_{15}\) have larger dissociation energies compared to those with AlC\(_{11}\)F\(_{15}\), which reflects higher Lewis acidity of fluorinated boron-containing pyramidalized Lewis acids. Trends in bond dissociation enthalpies for phosphorus-containing complexes are similar to those of nitrogen analogues. Thus, perfluorinated group 13 adamantane derivatives form the most stable complexes with large dissociation energies and large dipole moments. Since dissociation enthalpies of complexes of EC\(_{11}\)F\(_{15}\) are much larger than that of AlCl\(_3\), perfluorinated adamantane derivatives are Lewis superacids in terms of Olah’s definition.

BP86/TZ2P level of theory. \(\Delta E\) The difference between values for fluorinated and non-fluorinated acceptors.
Due to high Lewis acidity, perfluorinated group 13 adamantane derivatives would be extremely difficult to isolate as free compounds, but synthesis of their complexes seems reliable. On the basis of bond angle–bond distance–bond energy relationship,[42,43] decrease of the C–E bond angle upon complex formation has been previously used as a quantitative indicator for the strength of the unstrained group 13 Lewis acids. However, for the rigid pyramidalized adamantane-type Lewis acids studied in the present work, the structural changes upon complex formation are very small. Fluorination of the acceptor moiety also has little effect on the structural parameters. Upon fluorination, B-X bond distances shorten by 0.066–0.068 Å with the only exception of the P(CH$_3$)$_3$ donor, B-C bond lengths increase by 0.003–0.027 Å, and C–B–C angles decrease by about 1.6–3.5°. For aluminum analogues, upon fluorination Al-X bond distances shorten by 0.085–0.116 Å, Al-C bond distances increase by 0.033–0.042 Å, and C–Al–C angles decrease by 4.8–5.3°.

Bonding analysis

In order to understand the origin of the higher stability of complexes of group 13 fluorinated adamantane derivatives we have undertaken an energy decomposition analysis (EDA) of the complexes in their closed shell ground state with respect to isolated fragments (Tables 2 and 3). The total bonding energies ($\Delta E$) for complexes with fluorinated acceptors are by 40.6–50.8 kcal mol$^{-1}$ larger compared to non-fluorinated. This difference mainly comes from the interaction energy ($\Delta E_{int}$), as deformation energies ($\Delta E_{def}$) favor hydrogen-substituted complexes (a maximum difference 7.4 kcal mol$^{-1}$). On the other hand, aluminum complexes present the same trends, but with smaller differences (Table 3). $\Delta E$ differences are in the range 20.7–32.2 kcal mol$^{-1}$, and $\Delta E_{def}$ also favor hydrogenated systems with a maximum difference of 4.5 kcal mol$^{-1}$. Thus, we must go into the decomposition of $\Delta E_{int}$ into Pauli, electrostatic and orbital interaction terms in order to get an explanation for the larger strength of the bond formed in fluorinated complexes. Pauli repulsion does not give a clear trend, thus disfavoring fluorinated complexes with the exception of all B-P complexes and NH$_3$-BC$_9$H$_{15}$. For the same geometry, fluorinated compounds should have larger Pauli repulsion because they have more electrons. Lower Pauli repulsion for fluorinated compounds is attributed to their smaller $\alpha$(C-B-C) angles. In the cases that $\Delta E_{Pauli}$ favors the hydrogenated compounds, the contribution of this term to $\Delta E_{int}$ is minor, being up to 8.7 and 11.9 kcal mol$^{-1}$ for B and Al containing complexes, respectively.

Furthermore, in all these cases, both $\Delta V_{elstat}$ and $\Delta E_{oi}$ terms cause the largest contribution to the higher strength observed in fluorinated compounds. Only for B-P bonded compounds the decrease of Pauli repulsion upon fluorination makes this term more decisive than $\Delta V_{elstat}$. Therefore, we can state that stabilization of boron complexes with perfluorinated derivatives is mainly due to the orbital interaction term. On the other hand, as compared to boron analogues, aluminum-
containing complexes show a significant decrease of the absolute values of $\Delta E_{\text{elstat}}$, $\Delta E_{\text{diel}}$, and $\Delta E_{\text{Pauli}}$ due to the lengthening of Al-X bond and the lower electronegativity of Al. In general, stabilization of aluminum complexes with perfluorinated derivatives is due to a combination of more favorable $\Delta V_{\text{elstat}}$ and $\Delta E_{\text{diel}}$ terms.

With the aim to understand the orbital interactions referred above, the MO diagram for the complex NC$_{9}$H$_{15}$/C$_{1}$BC$_{9}$H$_{15}$ is shown in Figure 2. The MO diagrams for the other complexes are very similar (See HOMO and LUMO energies in Supporting Information, Table S4). As expected, the interaction between HOMO ($-4.49$ eV) of the donor fragment NC$_{9}$H$_{15}$ and LUMO ($-1.23$ eV) of the acceptor fragment BC$_{9}$H$_{15}$ leads to the formation of $\sigma$-bonding and $\sigma$-antibonding orbitals. Fluorination of the acceptor significantly decreases the energy of the LUMO (by 4.62 eV, from $-1.23$ to $-5.85$ eV), which enhances the stability of the complex.

Energy differences between the HOMO of the donor and the LUMO of the acceptor for Al containing compounds are smaller than for B containing ones (Table 4); the stabilization effect caused by fluorination is also noticeable. Thus, such stabilization of the LUMO by fluorination is translated into the larger orbital interactions observed above.

For all studied complexes there is a linear correlation between the energy difference of the HOMO of the donor $E_{\text{HOMO}}(D)$ and the LUMO of the acceptor $E_{\text{LUMO}}(A)$ (in eV) and the dissociation energy of the complex $\Delta E_{\text{diss}}$ [eq. (3), Fig. 3].

$$\Delta E_{\text{diss}} \text{(kcal mol}^{-1}\text{)} = (8.35 \pm 0.54) \{E_{\text{HOMO}}(D) - E_{\text{LUMO}}(A)\} + 53.1 \pm 1.6; \ R^2=0.91 \tag{3}$$

Importance of the frontier orbitals on the dissociation energy has been emphasized by Fleming,[45,46] however, the quantitative correlations for the donor–acceptor compounds like eq. (3) have not been reported.

| Dia   | BC$_{9}$H$_{15}$ | BC$_{9}$F$_{15}$ | AlC$_{9}$H$_{15}$ | AlC$_{9}$F$_{15}$ |
|-------|-----------------|-----------------|------------------|-------------------|
| NH$_3$| 127.61 (137.29) | 36.73 (46.99)   | 116.33 (125.81)  | 48.05 (57.76)     |
| N(CH$_3$)$_3$ | 106.48 (115.30) | 15.60 (25.00)   | 95.20 (103.82)   | 26.92 (35.77)     |
| NC$_{9}$H$_{15}$ | 95.15 (104.09) | 4.27 (13.79)    | 83.87 (92.61)    | 15.59 (24.56)     |
| PH$_3$ | 144.29 (153.82) | 53.41 (63.52)   | 133.01 (142.34)  | 64.73 (74.29)     |
| P(CH$_3$)$_3$ | 102.36 (111.16) | 11.48 (20.86)   | 91.08 (99.68)    | 22.80 (31.63)     |
| PC$_{9}$H$_{15}$ | 99.70 (108.69) | 8.82 (18.39)    | 88.42 (97.21)    | 20.14 (29.16)     |

Table 5. Standard enthalpies $\Delta H_{298}$ (in kcal mol$^{-1}$) and Gibbs energies $\Delta G_{298}$ (in parenthesis, in kcal mol$^{-1}$) for the process (4) in the gas phase.

Figure 4. The most stable configurations of the contact ion pairs in case of a) non-fluorinated; and b) perfluorinated Lewis acids.
Thermodynamics of hydrogen splitting

Enthalpies and Gibbs energies of the heterolytic hydrogen splitting in the gas phase (process (4)) are summarized in Table 5.

H₂ + D + A = [HD]⁺ + [HA]⁻  (4)

Optimized geometries of ionic products of hydrogen splitting are provided in the Supporting Information (Table S1).

The fluorination of the Lewis acid results in a dramatic decrease of the hydrogen splitting enthalpy by 90.9 and 68.3 kcal mol⁻¹ for complexes of BC₉F₁₅ with N(CH₃)₃ and NC₉H₁₅, respectively. The fluorination of the Lewis base NC₉H₁₅ makes the hydrogen splitting reaction slightly more exothermic (by about 2–6 kcal mol⁻¹). Our results indicate that the splitting of H₂ in gas-phase becomes energetically favorable if ion pair formation is taken into account.

Reaction energies ΔE° for the non-fluorinated compounds the most stable is the structure featuring dihydrogen bond (Fig. 4a). In the case of fluorinated derivatives, the ion pair in which terminal fluorine atoms are involved in intermolecular H…F interactions (Fig. 4b) is the most stable. Energetics of the hydrogen splitting with contact ion pair formation (process (5)) in the gas phase and in toluene solution are given in Table 6.

D + A + H₂ = [HD]⁺ ••• [HA]⁻  (5)

It should be noted that for weaker Lewis acids EC₉H₁₅, in several cases, optimization of the contact ion pair converged to the H₂ molecule, indicating favorability of hydrogen evolution. In contrast, for the perfluorinated group 13 adamantane derivatives the process (5) is highly exothermic. The solvent makes the hydrogen splitting reaction slightly more exothermic (by about 2–6 kcal mol⁻¹). Our results indicate that the splitting of H₂ in gas-phase becomes energetically favorable if ion pair formation is taken into account.

Reaction energies ΔE° for the non-fluorinated compounds the most stable is the structure featuring dihydrogen bond (Fig. 4a). In the case of fluorinated derivatives, the ion pair in which terminal fluorine atoms are involved in intermolecular H…F interactions (Fig. 4b) is the most stable. Energetics of the hydrogen splitting with contact ion pair formation (process (5)) in the gas phase and in toluene solution are given in Table 6.

**Table 6.** Reaction energies ΔE° (kcal mol⁻¹) for the process (5) in the gas phase and in toluene solution (in parenthesis).

| LA/LB | NH₃ | N(CH₃)₃ | NC₉H₁₅ |
|-------|-----|---------|---------|
| BC₉H₁₅ | [a] | 3.92 | 2.87 |
| BC₉F₁₅ | (−1.50) | (−1.9) |
| (−66.55) | (−72.48) | (−76.89) |
| AlC₉H₁₅ | [a] | (−4.2) |
| AlC₉F₁₅ | (−41.07) | (−48.75) | (−53.36) |
| (−41.79) | (−49.07) | (−53.05) |
| LA/LB | PH₃ | P(CH₃)₃ | PC₉H₁₅ |
|-------|-----|---------|---------|
| BC₉F₁₅ | (−27.91) | (−57.07) | (−55.95) |
| (−40.62) | (−66.90) | (−64.69) |
| AlC₉F₁₅ | [a] | (−40.43) | (−39.10) |
| (−17.28) | (−43.49) | (−40.93) |

Data for the most stable ion pair are given. BP86/TZ2P level of theory. [a] Optimization of the contact ion pair converges to the structure with molecular hydrogen molecule H₂.

**Table 7.** Reaction energies ΔE° (kcal mol⁻¹) for the process (6) in the gas phase and in toluene solution (in parenthesis).

| LA/LB | NH₃ | N(CH₃)₃ | NC₉H₁₅ |
|-------|-----|---------|---------|
| BC₉H₁₅ | [a] | 21.92 | 23.50 (17.70) |
| (10.96) | (11.62) | (13.62) |
| BC₉F₁₅ | (−4.67) | (−6.75) |
| (−11.82) | (−13.62) |
| AlC₉H₁₅ | [a] | 24.65 (19.64) |
| AlC₉F₁₅ | 7.07 | 7.83 |
| (9.56) | (2.67) |
| (3.06) |
| LA/LB | PH₃ | P(CH₃)₃ | PC₉H₁₅ |
|-------|-----|---------|---------|
| BC₉H₁₅ | [a] | 13.70 | 15.04 |
| (21.28) | (4.65) |
| (6.48) |
| AlC₉H₁₅ | [a] | 15.59 |
| AlC₉F₁₅ | 13.17 |
| (22.51) | (6.72) |
| (9.34) |

Data for the most stable ion pair are given. BP86/TZ2P level of theory. [a] Optimization of the contact ion pair converges to the structure with molecular hydrogen molecule H₂.

Conclusions

A comparative computational study of the structural properties, stability and reactivity of adamantane-based Lewis acids and their donor–acceptor complexes has been carried out. Fluorination dramatically decreases the LUMO energy of the acceptor and increases the Lewis acidity, making group 13 perfluorinated adamantane derivatives Lewis superacids. EDA results show that stronger orbital interactions are responsible for the larger stability of boron complexes with fluorinated acceptors. In the case of aluminum complexes, the higher stability of...
the perfluorinated compounds is attributed to a combination of more favorable electrostatic and orbital interaction terms. For all studied complexes there is a linear correlation between the energy difference of HOMO of the donor and LUMO of the acceptor molecule and the dissociation energy of the complex.

Finally, our results demonstrate that the fluorination of the Lewis acid has tremendous effect on the hydrogen splitting process. Perfluorinated 1-boroadamantane in combination with N-containing donors is predicted to exothermically split molecular hydrogen with the formation of the contact ion pairs. Thus, perfluorinated 1-boroadamantane appears to be an attractive synthetic target as Lewis superacid and a good candidate for the construction of spatially separated donor–acceptor cryptands.

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Keywords: donor–acceptor complexes · boron · aluminum · bonding analysis · EDA · hydrogen splitting

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Additional Supporting Information may be found in the online version of this article.

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