Inorganic Chemistry
Article

*Inorg. Chem.* **2009**, *48*, 8145–8153 **8145**
DOI: 10.1021/ic900270c

# Donor−Acceptor "Dressing" of "Naked" Group 13−15 Cubanes

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Received February 9, 2009

The structures and stability of the group 13−15 inorganic cubane clusters, stabilized by donor−acceptor interactions, are theoretically explored at the B3LYP/TZVP level of theory. $[DMYA]_4$ compounds (M, Y = group 13 and 15 elements; D, A = donor and acceptor molecules $NH_3$ and $BH_3$, respectively) are predicted to be true minima on the potential energy surface. It is shown that donor−acceptor "dressing" significantly stabilizes "naked" $[MY]_4$ cubanes. Possible synthetic approaches and potential uses of these novel $[DMYA]_4$ compounds as single-source precursors to group 13−15 materials are discussed.

## Introduction

Group 13−15 binary compounds and composites are prospective materials for the microelectronic industry.[1] The formation of stoichiometric compounds in a controlled fashion requires the use of single-source precursors (SSPs). Precursor chemistry has become important for the success of materials science, especially in microelectronics. Group 13−15 donor−acceptor (DA) complexes,[1] as well as oligomeric ring and cluster compounds,[2,3] have been successfully utilized as SSPs to 13−15 materials. Because all examined SSPs feature at least one terminal group (organic radical or halogen) on the 13 and 15 centers, their conversion to the bulk 13−15 material requires clean stripping of the terminal groups. Incomplete terminal group removal at elevated temperatures results in carbon or halogen contamination of the obtained product. From this point of view, ideal SSPs for 13−15 binary and composite materials would be "naked" $[MY]_n$ clusters, which do not contain any terminal groups. Although small $[MY]_n$ clusters are experimentally observed upon laser vaporization of 13−15 materials,[4−7] such clusters are highly reactive. To date, there are no examples of the individual $[MY]_n$ clusters stable at room temperature.

In order to stabilize "naked" $[MY]_n$ clusters, they can be effectively "dressed up" by means of DA interactions with Lewis acids and bases. DA stabilization of 13−15 bonded derivatives is well-known.[8−10] However, there is no theoretical/experimental study on the DA stabilization of naked 13−15 cubanes. Utilization of the DA stabilization approach allowed Scheer et al.[8] to isolate and characterize a series of complexes of such reactive monomers as $H_2MYH_2$ (M = B, Al, Ga; Y = P, As), including borane-stabilized $BH_3PH_2BH_2NMe_3$.[8d] Very recently, controlled synthesis of a DA-stabilized ladder-type compound (Scheme 1c) featuring the edge of the DA-stabilized cube was reported by Bodensteiner et al.[11] In the present report, stabilization of the "naked" 13−15 clusters $[MY]_n$ by DA interactions is addressed for the first time from the theoretical point of view. In principle, a whole series of $[DMYA]_n$ compounds are theoretically possible, but in the present report, only stabilization of tetrameric compounds $[MY]_4$ has been considered. Tetramers $[MY]_4$ are observed upon laser vaporization of 13−15 binary

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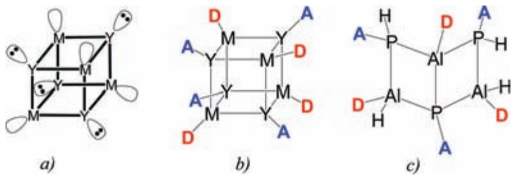
**Scheme 1.** Schematic Representation of (a) the Lone Pairs and Vacant Orbitals of "Naked" $[MY]_4$ Cubanes; (b) Proposed DA-Dressed Cubanes $[DMYA]_4$; and (c) the Ladder-Type Compound Reported by Bodensteiner et al.[11] [A = $W(CO)_5$; D = $NMe_3$]



compounds, but their low concentration in the laser beam precludes detailed studies of their structures. It should be noted that among closely related 13−15 oligomer compounds $[RMYR']_n$ cubic tetramers $[RMYR']_4$ and drum-type hexamers $[RMYR']_6$ are the most abundant.[2]

In the present report, the structures and stability of 13−15 DA-dressed cubanes $[DMYA]_4$ (Scheme 1b) will be discussed. Possible synthetic pathways of their formation are proposed and examined, and their potential as SSPs toward 13−15 composite materials is also discussed. In order to reduce the computational costs, simple donor and acceptor molecules (ammonia and borane, respectively) have been chosen for the case study. Despite their simplicity, they represent adequate approximations for the "real-world" compounds. As an example, $PH_2BH_2$, stabilized by $BH_3$ and $NMe_3$, has been isolated and structurally characterized by Schwan et al.[8d] Results obtained in the present work may be generalized for any combination of stabilizing Lewis acids and bases.

## Computational Details

All structures were fully optimized and verified with subsequent vibrational analysis to be minima on their respective potential energy surfaces (PESs). Density functional theory (DFT) in the form of a hybrid B3LYP functional[12] was used together with the full-electron triple-ζ-quality TZV basis set of Ahlrichs,[13] augmented by d-type polarization functions (TZVP). For hydrogen, a standard 6-311G** basis set was employed. The *Gaussian03* suite of programs[14] was used throughout. The B3LYP functional usually gives a good prediction of the thermodynamic properties for group 13−15 elements, including DA bond formation.[15,16] Gilbert[17] reported that the B−N bond energies in molecular complexes of $BR_3$ (R = H,$CH_3$) with ammonia and methylamines are significantly underestimated at the B3LYP/6-311++G(d,p) level of theory. Large cumulative errors for the B3LYP method have also been observed for the enthalpies of formation of hydrocarbons and C−C bond dissociation reactions.[18] For recent discussions on the performance of the B3LYP and other DFT methods and the origin of such errors, see the works of Schleyer et al.[19] and Grimme[18] and references cited therein. Recently, it was demonstrated[20] that the basis set has an influence on the performance of the B3LYP method for energetics of DA interactions between 13 and 15 Lewis acids and bases. Medium-sized basis sets yield better agreement with the experimental results because of the fortuneous cancellation of errors between the basis set deficiency and the medium-range electron correlation treatment.

## Results and Discussion

**Structures of the "Naked" $[MY]_4$ Cubanes.** Clusters of group 13−15 elements with $[MY]_4$ composition have been extensively studied theoretically.[21] Although cubane structures are not always the most favorable among $[MY]_4$ isomers, in the present report, our primary interest relies on the DA stabilization of the cubane-type isomers; therefore, only structures of the "naked" cubanes $[MY]_4$ will be considered here. A detailed discussion on the structures and stability of different $[MY]_4$ isomers can be found in the literature.[21]

Structural features of the studied cubanes are presented in Figure 1, and the most important MY distances are summarized in Table 1. With the single exception of $[GaN]_4$, where a $T_d$-symmetric structure was found to be a third-order stationary point, all other $T_d$-symmetric cubanes $[MY]_4$ are true minima on PESs. Lowering the symmetry allowed one to obtain a $C_s$-symmetric cubane-type structure of the $[GaN]_4$ cluster, which is only by 12 kJ $mol^{-1}$ lower in energy compared to the $T_d$-symmetric

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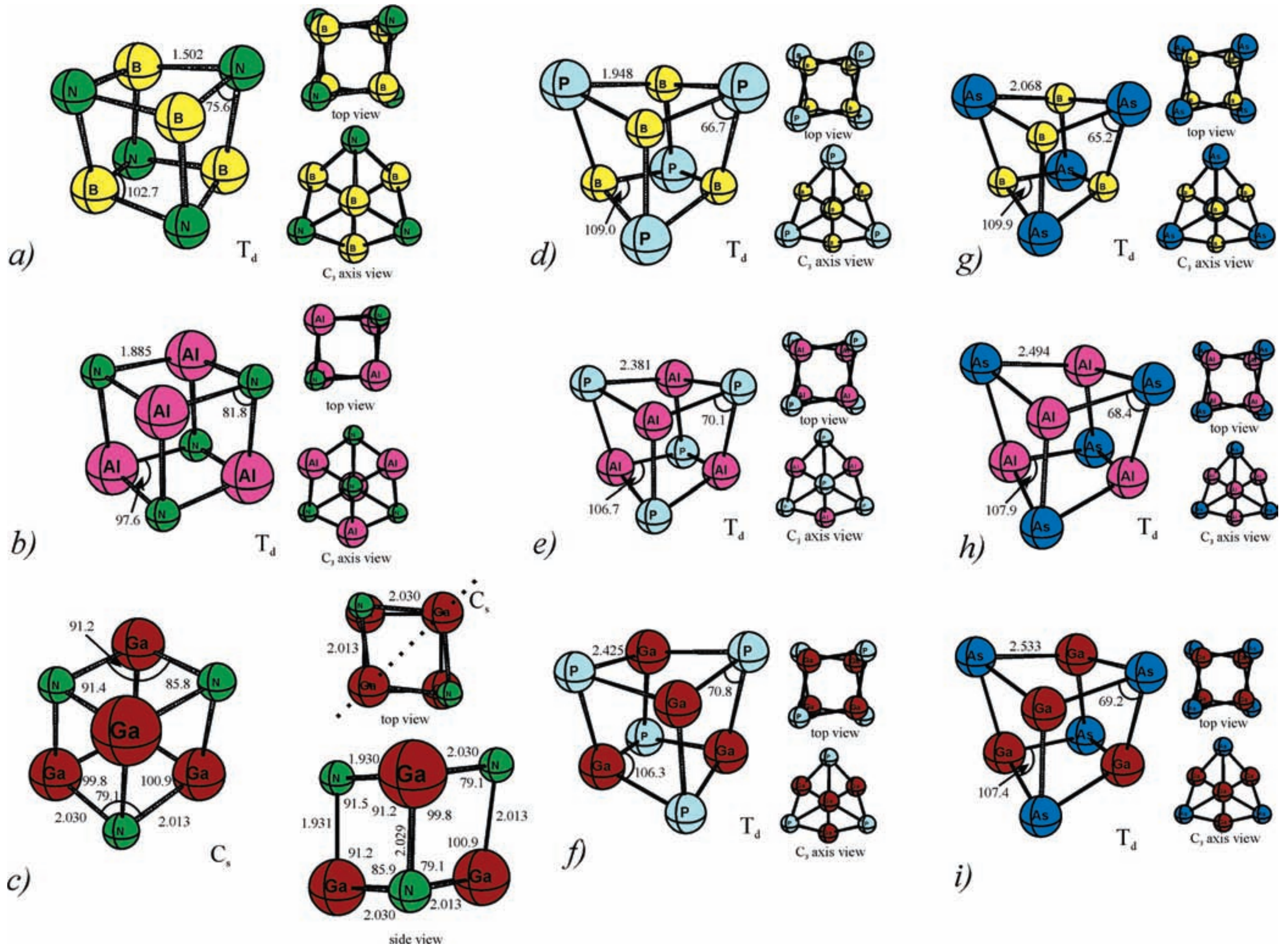

**Figure 1.** Optimized structures of the naked $[MY]_4$ cubanes: (a) $[BN]_4$; (b) $[BP]_4$; (c) $[BAs]_4$; (d) $[AlN]_4$; (e) $[AlP]_4$; (f) $[AlAs]_4$; (g) $[GaN]_4$ ($C_s$ point group); (h) $[GaP]_4$; (i) $[GaAs]_4$.

**Table 1.** Optimized MY Distances in the $T_d$-Symmetric "Naked" Cubanes $[MY]_4$, Donor and DA-"Dressed" $[(NH_3)MY]_4$ and $[(NH_3)MY(BH_3)]_4$ Cubanes, Classical $[HMYH]_4$ Cubanes, and DA Complexes $H_3MYH_3$ Using the B3LYP/TZVP Level of Theory

| | $[MY]_4$ | $[(NH_3)MY]_4$ | | $[(NH_3)MY(BH_3)]_4$ | | | $[HMYH]_4$[d] | $H_3MYH_3$ |
|---|---|---|---|---|---|---|---|---|
| M−Y | r(M−Y) | r(M−Y) | r($H_3N$−M) | r(M−Y) | r($H_3N$−M) | r(Y−$BH_3$) | r(M−Y) | r(M−Y) |
| B−N | 1.502 | 1.555 | 1.633 | 1.562 | 1.556 | 1.575 | 1.595 | 1.665 |
| Al−N | 1.885 | 1.899 | 2.026 | 1.869−1.928[b] | 1.946[b] | 1.592[b] | 1.940 | 2.093 |
| Ga−N | 1.930−2.030[a] | 1.996 | 2.134 | 1.945−1.995[c] | 2.008[c] | 1.583[c] | 2.004 | 2.192 |
| B−P | 1.948 | 2.017 | 1.624 | 1.998 | 1.595 | 1.998 | 2.028 | 1.958 |
| Al−P | 2.381 | 2.390 | 2.051 | 2.381 | 2.030 | 2.084 | 2.438 | 2.585 |
| Ga−P | 2.425 | 2.428 | 2.175 | 2.411 | 2.118 | 2.050 | 2.449 | 2.611 |
| B−As | 2.068 | 2.129 | 1.619 | 2.118 | 1.598 | 2.134 | 2.138 | 2.104 |
| Al−As | 2.494 | 2.495 | 2.059 | 2.482 | 2.040 | 2.224 | 2.535 | 2.705 |
| Ga−As | 2.533 | 2.531 | 2.193 | 2.510 | 2.134 | 2.191 | 2.542 | 2.735 |

[a] $C_s$ point group. [b] $C_2$ point group. [c] $S_4$ point group. [d] Results from ref 22.

third-order stationary point. Note, however, that according to BelBruno,[21j] Wu et al.,[21r] and Qu and Bian,[21s] a planar $D_{4h}$-symmetric ring is the lowest-energy structure of $Ga_4N_4$, while the structure featuring the azido group $N_3$ was found to be the most stable by Pandey et al.[21q] and Tafipolsky and Schmid.[21t]

Cluster cores are generally highly distorted with respect to the ideal cube. Valence angles at P and As centers lie in the range 65−71°, and for the N centers, they are in the range 76−91°. For the $C_s$-symmetric $[GaN]_4$, the Ga−N bond lengths are unequivalent and lie in the range 1.93−2.03 Å and the Ga−N−Ga and N−Ga−N valence angles are in the ranges 79−92° and 91−101°, respectively.

**Structures of the DA-"Dressed" $[DMYA]_4$ Cubanes.** Initial structure optimizations have been carried out in the framework of the $T_d$ point group. With the exception of $[(NH_3)AlN(BH_3)]_4$ and $[(NH_3)GaN(BH_3)]_4$, all $T_d$-symmetric cubanes are predicted to be true minima on PES. Optimization of $[(NH_3)AlN(BH_3)]_4$ and $[(NH_3)GaN(BH_3)]_4$ without symmetry constraints resulted in $C_2$- and $S_4$-symmetric structures, respectively (Figure 2b, c). The driving force of this distortion is probably the

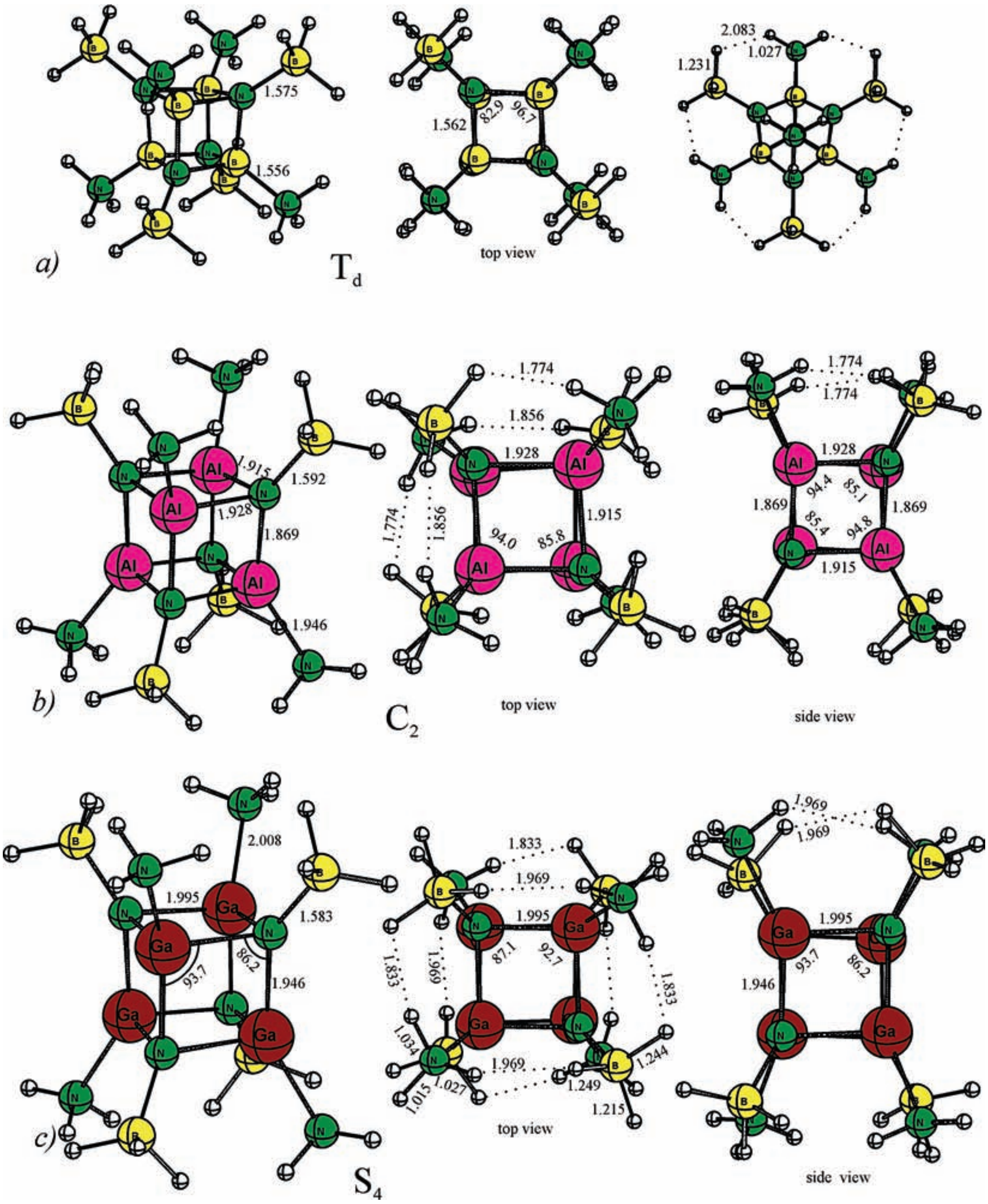

**Figure 2.** Optimized structures of the N-containing DA-dressed cubanes (a) $[(NH_3)BN(BH_3)]_4$, (b) $[(NH_3)AlN(BH_3)]_4$, and (c) $[(NH_3)GaN(BH_3)]_4$.

formation of intramolecular H···H interactions (so-called "dihydrogen" bonds). Both compounds exhibit short intramolecular B−H···H−N contacts of 1.774−1.969 Å, which can be compared to those predicted theoretically for the ammonia borane oligomers $[H_3BNH_3]_n$ (1.952−2.329 Å).[23,24] Especially short B−H···H−N distances of 1.774 Å are found in $[(NH_3)AlN(BH_3)]_4$ (Figure 2b). These distances are close to the shortest experimentally known dihydrogen bonds (which are in the range 1.7−2.2 Å[25]). Note that $T_d$-symmetric $[(NH_3)BN(BH_3)]_4$ has much longer B−H···H−N distances of 2.080 Å. The finding that only Al−N- and Ga−N-containing cubanes adopt distorted structures may come from the fact that distortion of Al, Ga, and N centers (pyramidalization and planarization) is significantly less demanding energetically compared to their B, P, and As counterpairs.[26] Thus, exothermicity of the formation of eight intramolecular dihydrogen bonds B−H···H−N is sufficient to compensate for unfavorable structural distortions for the Al−N and Ga−N cages.

All P and As analogs adopt highly symmetric structures ($T_d$ point group; Figure 3) that are true minima on PES. Because of the larger size of the cubane core, terminal donor and acceptor molecules are not so close

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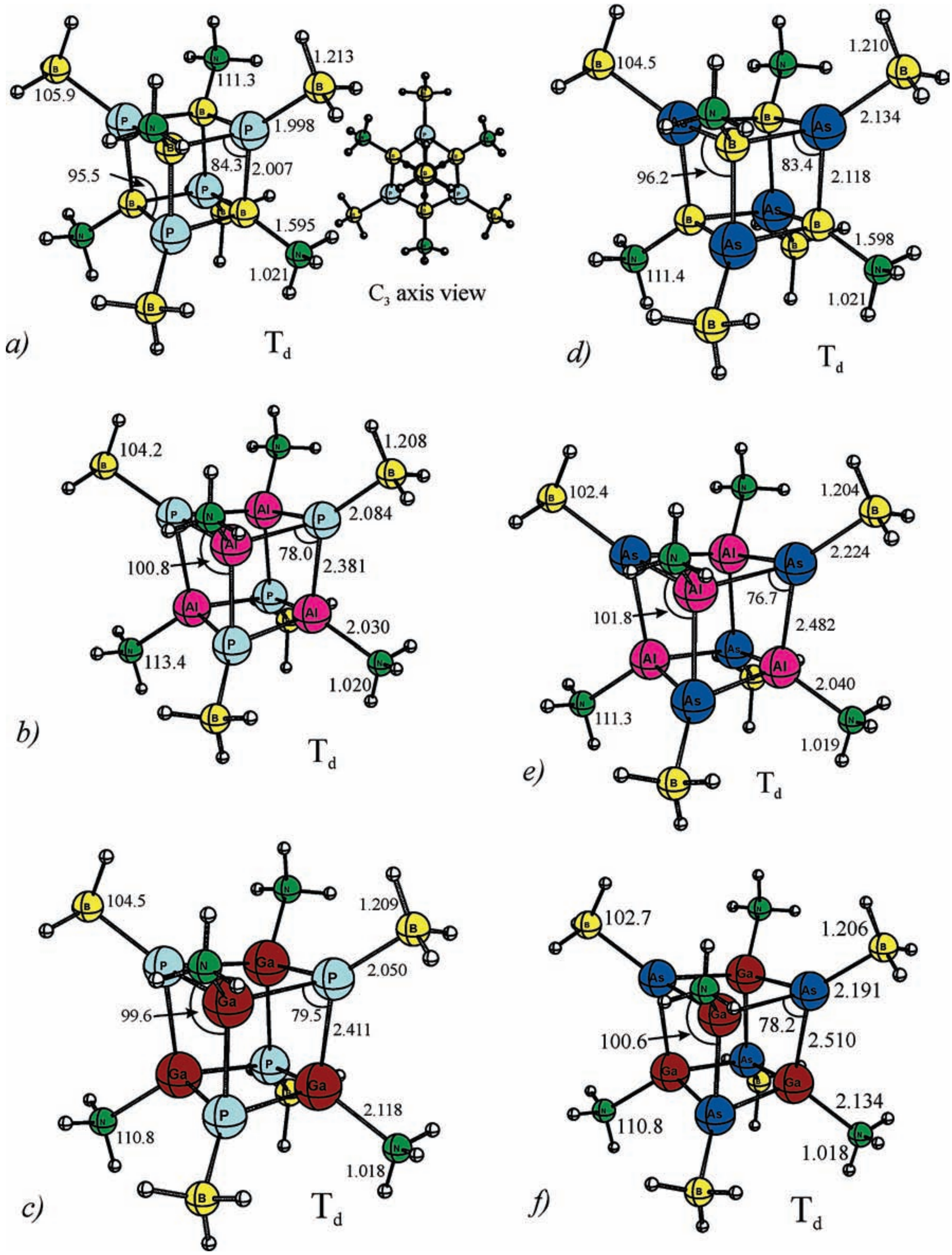


**Figure 3.** Optimized structures of the $T_d$-symmetric DA-dressed cubanes (a) $[(NH_3)BP(BH_3)]_4$, (b) $[(NH_3)AlP(BH_3)]_4$, (c) $[(NH_3)GaP(BH_3)]_4$, (d) $[(NH_3)BAs(BH_3)]_4$, (e) $[(NH_3)AlAs(BH_3)]_4$, and (f) $[(NH_3)GaAs(BH_3)]_4$.

together and there are no noticeable "dihydrogen" bonds formed (B−H···H−N distances are larger than 3.6 Å).

Bonding in $[DMYA]_4$ clusters can be depicted as the group 15 element having a formal oxidation state 3 and possessing one lone pair, which can be used for the DA stabilization (Scheme 1a). DA bond distances $BH_3$−Y and $NH_3$−M in the cubanes are comparable to those found in simple 13−15 adducts $H_3MYH_3$ (Table 1). Data in Table 1 show that, upon dressing, the M−Y distances in the cluster core exhibit few changes. B−Y bonds increase by about 0.05 Å, while Al−Y and Ga−Y bonds remain the same or only marginally decrease (by 0.02 Å). The predicted Al−P distance in $[(NH_3)AlP(BH_3)]_4$ of 2.381 Å is close to the central Al−P distance of 2.394(3) Å found in the experimentally synthesized ladder compound.[11]

Mulliken population analysis (Table 2) shows that each $BH_3$ accepts about 0.36−0.45e (total charge accepted 1.44−1.8e), while each $NH_3$ donates 0.29−0.56e (total 1.2−2.2e). As a result, the net change in the electron density in the $M_4Y_4$ core is small. For more electronegative B compounds, the $B_4Y_4$ fragment carries a negative charge (−0.37 to −0.47e), while for Al and Ga analogues, the $M_4Y_4$ fragment is positively charged (0.14−0.55e). Thus, in both cases, $M_4Y_4$ is primarily serving as a charge-transfer medium from donor ($NH_3$) to acceptor ($BH_3$) molecules.

**Stability of the DA-"Dressed" [DMYA]$_4$ Cubanes.** The thermodynamic characteristics of the dissociation of $[(NH_3)MY(BH_3)]_4$ into "naked" $[MY]_4$ cubanes and DA complex $BH_3NH_3$ (process 1) are given in Table 3.

$$[(NH_3)MY(BH_3)]_4 = [MY]_4 + 4BH_3NH_3 \qquad (1)$$

The energy of formation of two DA bonds (with donor $NH_3$ and acceptor $BH_3$ molecules) fully compensates for unfavorable breaking of one B−N DA bond in the $BH_3NH_3$. Process (1) of the cubane undressing is highly endothermic but favorable by entropy, and therefore $[DMYA]_4$ will be stable with respect to the stripping of the donor and acceptor molecules at low temperatures. Note that the stability of the DA-dressed cubanes with respect to dissociation according to eq 1 decreases in the order AlN > BN > GaN ≫ BP > AlP > BAs > AlAs > GaP > GaAs. Dissociation is thermodynamically allowed only at higher temperatures (1360−1700 K for N-containing cubanes and 290−750 K for P and As analogues). Computations predict that dissociation of $[(NH_3)GaAs(BH_3)]_4$ will be favorable already above 290 K. In contrast, $[(NH_3)AlP(BH_3)]_4$ is predicted to be stable with respect to dissociation into gaseous $BH_3NH_3$ and $[AlP]_4$ until 750 K.

**Table 2.** Partial Charges on Fragments According to Mulliken Population Analysis (B3LYP/TZVP Level of Theory)

| | $[(NH_3)MY]_4$ | | $[(NH_3)MY(BH_3)]_4$ | | |
|---|---|---|---|---|---|
| M−Y | $q(NH_3)$ | $q(M_4Y_4)$ | $q(NH_3)$ | $q(BH_3)$ | $q(M_4Y_4)$ |
| B−N | 0.484 | −1.936 | 0.502 | −0.384 | −0.470 |
| Al−N | 0.310 | −1.238 | 0.344 | −0.379 | 0.140 |
| Ga−N | 0.231 | −0.924 | 0.313 | −0.358 | 0.181 |
| B−P | 0.487 | −1.948 | 0.556 | −0.439 | −0.471 |
| Al−P | 0.283 | −1.130 | 0.324 | −0.413 | 0.356 |
| Ga−P | 0.229 | −0.916 | 0.287 | −0.424 | 0.547 |
| B−As | 0.493 | −1.972 | 0.535 | −0.448 | −0.345 |
| Al−As | 0.273 | −1.092 | 0.307 | −0.392 | 0.340 |
| Ga−As | 0.209 | −0.836 | 0.268 | −0.400 | 0.530 |

The large endothermicity of process (1) is mostly due to the low stability of the "naked" $[MY]_4$ cubanes themselves. Although thermodynamically feasible, the direct synthesis of $[DMYA]_4$ via reactions of $[MY]_4$ with Lewis acids and bases is not expected to be practically realized because of the low stability of the "naked" $[MY]_4$ cubanes.

Therefore, alternative synthetic approaches toward DA-dressed cubanes should be developed. One of such ways would be a displacement reaction starting from $[RMYR']_4$ cubanes. In the present report, H-containing $[HMYH]_4$ were considered as model compounds for such displacement reactions. The gas-phase reaction of "substitution" of the terminal H atoms by DA groups (reaction 2) is entropically unfavorable for all 13−15 pairs, and therefore the enthalpy factor should be decisive.

$$[HMYH]_4 + 4BH_3NH_3 = [(NH_3)MY(BH_3)]_4 + 4H_2 \qquad (2)$$

Process (2) is exothermic only for B−N, Al−P, and Al−As 13−15 pairs, for which it is allowed thermodynamically at low temperatures. Of course, even if the direct reaction of $[RMYR']_4$ cubanes with DA compounds is allowed thermodynamically, it may require significant activation energy for M−R and Y−R bond cleavage.

A more practical approach starts from the DA complexes $D{-}MH_3$ and $H_3Y{-}A$ and includes stepwise $H_2$ elimination with the formation of DA-stabilized amido and imido compounds as reactive intermediates (Scheme 2). The overall process is presented by eq 3.

$$D{-}MH_3 + H_3Y{-}A = \frac{1}{4}[DMYA]_4 + 3H_2 \qquad (3)$$

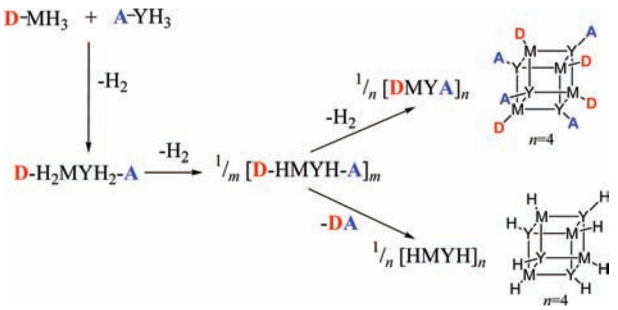
Note that the synthesis of monomeric $DH_2MYH_2A$ intermediate species has been realized by Scheer (with A = $BH_3$, $Cr(CO)_5$, $W(CO)_5$; D = $NMe_3$; M = B, Al; Y = P, As).[8] Quantum-chemical computations revealed that $H_2$ elimination is exothermic; the activation energy for the first $H_2$ elimination does not depend on the nature of stabilizing donor and acceptor molecules.[8c]

**Table 3.** Thermodynamic Characteristics for the Gas-Phase Processes (B3LYP/TZVP Level of Theory)[a]

| | process (1) | | | process (2) | | | process (3) | | | process (4) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| M−Y | $\Delta H°_{298}$ | $\Delta S°_{298}$ | $\Delta G°_{298}$ | $\Delta H°_{298}$ | $\Delta S°_{298}$ | $\Delta G°_{298}$ | $\Delta H°_{298}$ | $\Delta S°_{298}$ | $\Delta G°_{298}$ | $\Delta H°_{298}$ | $\Delta S°_{298}$ | $\Delta G°_{298}$ |
| B−N | 924 | 630 | 736 | −19 | −134 | 21 | −26 | 60 | −44 | −21 | 94 | −49 |
| Al−N | 1055 | 620 | 871 | 153 | −138 | 194 | −67 | 45 | −80 | −105 | 79 | −129 |
| Ga−N | 897 | 658 | 701 | 335 | −132 | 375 | 61 | 44 | 48 | −23 | 77 | −46 |
| B−P | 399 | 576 | 227 | 31 | −84 | 57 | 71 | 60 | 53 | 64 | 81 | 39 |
| Al−P | 361 | 479 | 218 | −13 | −24 | −6 | −39 | 69 | −60 | −36 | 75 | −59 |
| Ga−P | 251 | 499 | 103 | 81 | −25 | 88 | −17 | 65 | −36 | −37 | 71 | −58 |
| B−As | 328 | 580 | 155 | 34 | −82 | 59 | 66 | 56 | 50 | 58 | 76 | 35 |
| Al−As | 260 | 482 | 116 | −54 | −27 | −46 | −77 | 64 | −96 | −63 | 70 | −84 |
| Ga−As | 141 | 493 | −5.5 | 31 | −12 | 35 | −65 | 64 | −84 | −73 | 67 | −93 |

[a] (1) $[(NH_3)MY(BH_3)]_4 = [MY]_4 + 4H_3BNH_3$; (2) $[HMYH]_4 + 4H_3BNH_3 = [(NH_3)MY(BH_3)]_4 + 4H_2$; (3) $H_3N\text{-}MH_3 + H_3Y\text{-}BH_3 = {}^1/_4[(NH_3)MY(BH_3)]_4 + 3H_2$; (4) $H_3NMH_3 + H_3YBH_3 = {}^1/_4[HMYH]_4 + 2H_2 + H_3BNH_3$. Standard enthalpies $\Delta H°_{298}$ and standard Gibbs energies $\Delta G°_{298}$ are in kJ mol$^{-1}$, and standard entropies $\Delta S°_{298}$ are in J mol$^{-1}$ K$^{-1}$.

**Scheme 2.** Generalized Reaction Pathway Leading to the DA-Stabilized $[DMYA]_n$ Clusters



Thermodynamic characteristics show that the formation of $[DMYA]_4$ tetramers is endothermic for Ga−N, B−P, and B−As systems and exothermic and entropically favorable for other 13−15 pairs. Thus, process (3) appears to be a viable reaction path for the generation of all Al-containing compounds, as well as B−N, Ga−P, and Ga−As compounds.

It is known that elimination of the last terminal groups from $[RMYR']_n$ compounds requires elevated temperatures (see ref 2 and references cited therein). Therefore, elimination of the last 1 mol of $H_2$ may be in concurrence with the DA elimination and formation of $[HMYH]_4$ (shown in Scheme 2, bottom right).

$$D-MH_3 + H_3Y-A = \frac{1}{4}[HMYH]_4 + 2H_2 + DA \quad (4)$$

The overall reaction of the formation of $[HMYH]_4$ from the DA complexes $D-MH_3$ and $H_3Y-A$ [process (4)] is exothermic for most M−Y pairs, with the exception of B−P and B−As, for which it is endothermic because of the low stability of tetramers $[HBPH]_4$ and $[HBAsH]_4$, respectively. Thus, processes (3) and (4) are competitive from the thermodynamic point of view. In such a situation, kinetic factors will play a significant role.

Barriers for the experimentally observed first intermolecular $H_2$ elimination from starting compounds $D-MH_3$ and $PH_3-A$ to form $DH_2MPH_2A$ (D = $NH_3$, $NMe_3$, Py, dmap; A = $BH_3$, $Cr(CO)_5$) were predicted to be 141 and 172 kJ $mol^{-1}$ for M = Al and Ga, respectively[8c] and not to depend much on the nature and size of the donor and acceptor molecules. Pathways of $H_2$ elimination from closely related 13−15 DA complexes have been extensively studied theoretically by Dixon[28−34] and McKee.[35,36] Their results show that there are very wide ranges of reaction pathways operational for $H_2$ elimination (intramolecular, acceptor-assisted), with the lowest activation energies ranging from 113 to 150 kJ $mol^{-1}$. These barriers are comparable to or even lower than those reported for the intermolecular interactions. Because the first dehydrogenation reaction effectively operates via an intermolecular $H_2$ elimination pathway,[8c] the following dehydrogenation reactions are also expected to be operational because they are associated with similar or smaller barriers. Note that for the DA-protected Al−P system $H_2$ elimination easily proceeds at room temperature,[11] which suggests very little kinetic limitation of the dehydrogenation process for the reaction in solution. It seems that the kinetic factor will not place a limit for the synthesis of the DA-stabilized cubanes via a $H_2$ elimination pathway.

On the other hand, removal of the supporting donor and acceptor molecules requires breaking of the two relatively strong DA bonds (sum of the dissociation energies of $M-NH_3$ and $Y-BH_3$ bonds of 115−190 kJ $mol^{-1}$).[27] Note that for 13−15 DA complexes dissociation proceeds without additional barriers beyond the reaction endothermicity. Usually, dissociation of 13−15 complexes with strong donors and acceptors requires elevated temperatures, and $H_2$ elimination is expected to occur at much lower temperatures.

Thus, among the pathways considered for the synthesis of $[DMYA]_n$, stepwise $H_2$ elimination, according to Scheme 2, appears to be the most promising. The best synthetic targets for practical realization, according to computations, are those based on Al-containing compounds (Al−N and Al−P systems). These theoretical results are in good agreement with the recent room-temperature synthesis of Al−P-based donor-stabilized trimeric and ladder structures by Bodensteiner et al.[11]

As for the potential as SSPs toward 13−15 materials, proposed $[(NH_3)MY(BH_3)]_4$ compounds are entirely composed from group 13 and 15 elements and hydrogen. If desired, doping of such 13−15 materials with additional elements in a controlled way could be achieved by changing the nature of the Lewis acids and bases used as acceptor or donor fragments. Thus, dressed cubanes are of potential interest as SSPs for the 13−15 composites with controlled stoichiometry. Reactive carrier gases, such as ammonia, may significantly facilitate the removal of terminal acceptor molecules and help with the conversion of the precursor to the final material. However, as we were reminded by one of the reviewers, in order to be practically applicable as SSPs, compounds should also have sufficient volatility and long-term stability and be easily available in large-scale quantities.

On the basis of the results of the present study, the synthetic pathway of the $H_2$ elimination shown in Scheme 2 seems worth experimental attempts, especially for the Al-based systems. Predicted harmonic vibrational frequencies and IR intensities for the "naked" and "dressed" cubanes are summarized in the Supporting Information (Tables 3S−5S) and may help in the experimental identification of the compounds.

The results obtained in the present work for the stabilization of simple $[MY]_4$ cubane tetramers may be generalized for the other $[MY]_n$ oligomers as well. Therefore,

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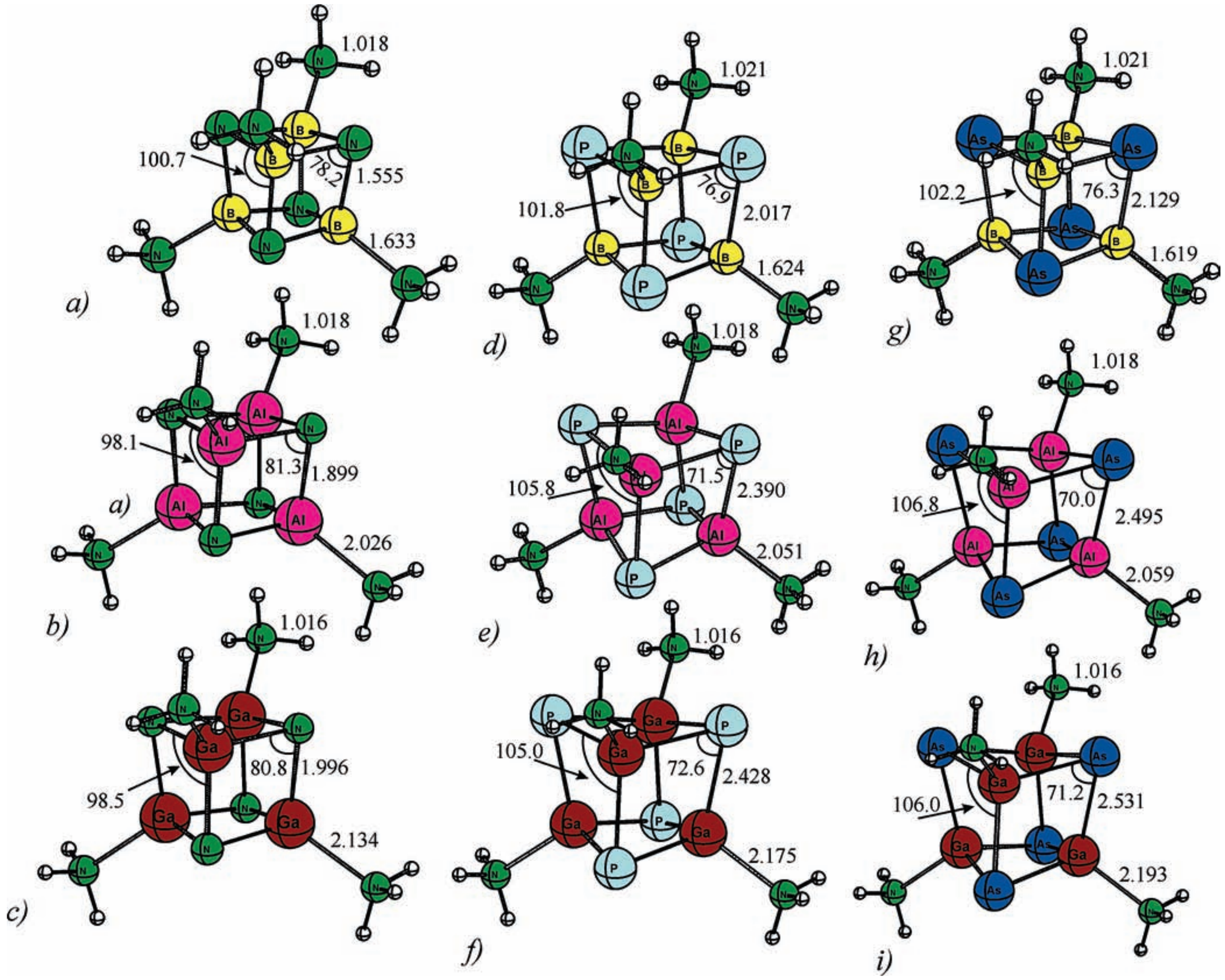

**Figure 4.** Optimized structures of the $T_d$-symmetric donor-stabilized cubanes (a) $[(NH_3)BN]_4$, (b) $[(NH_3)BP]_4$, (c) $[(NH_3)BAs]_4$, (d) $[(NH_3)AlN]_4$, (e) $[(NH_3)AlP]_4$, (f) $[(NH_3)AlAs]_4$, (g) $[(NH_3)GaN]_4$, (h) $[(NH_3)GaP]_4$, and (i) $[(NH_3)GaAs]_4$.

it is expected that DA-stabilized oligomers $[DMYA]_n$ may become viable synthetic targets. Because the size of the substituents R is the major factor determining the oligomerization degree of closely related $[RMYR']_n$ compounds (bulkier terminal groups R and R′ result in smaller $n$),[2] a similar effect is expected for the oligomerization degree of $[DMYA]_n$ compounds. Thus, the oligomerization degree $n$ in Scheme 2 is expected to be determined by the size of the donor and acceptor molecules. A recently reported "half-cube" ladder compound was stabilized by bulky $W(CO)_5$ acceptors. It is expected that less sterically demanding Lewis acids may result in cubane-type compounds. By analogy with the most abundant $[RMYR']_{4,6}$ species,[2] the most expected are structures with oligomerization degrees 4 and 6 ("dressed" cubane and drum-type compounds $[DMYA]_{4,6}$). If made, such compounds are expected to serve as excellent SSPs for the controlled synthesis of 13−15 materials.

**Donor-Stabilized Cubanes.** Recently, it was demonstrated that donor-only ($NMe_3$) stabilization is sufficient to stabilize monomeric $BH_2PH_2$.[8d] In this regard, the possibility of donor-only stabilization of $[MY]_4$ cubanes has been addressed. To this end, structures of $[(NH_3)MY]_4$ have been fully optimized in the framework of the $T_d$ point group. All obtained structures are true minima on PESs (Figure 4). All DA bond lengths in donor-stabilized adducts are longer compared to DA-stabilized ones. Mulliken population analysis (Table 2) shows that in B-containing cubanes the $B_4Y_4$ unit carries large negative charges (−1.94 to −1.97e). This may be attributed to the larger electronegativity of B as compared to heavier group 13 elements (the net negative charge of $M_4Y_4$ for Al- and Ga-containing cubanes is only −0.84 to −1.24e). Upon complexation with four Lewis acids $BH_3$, the absolute charge on the $M_4Y_4$ core becomes significantly smaller, while the donor ability of each $NH_3$ molecule is enhanced by 0.02−0.08e. The total charge accepted by four $BH_3$ molecules is 1.43−1.79e.

The thermodynamic characteristics of major processes are summarized in Table 4. It is interesting to note that the process of the formation of only a donor-stabilized compound from $D{-}MH_3 + YH_3$ is favorable for Al−P, Ga−P, Al−As, and Ga−As systems. Thus, in the case of P- and As-containing cubanes, the interaction with donor molecules only already provides significant energetic

**Table 4.** Thermodynamic Characteristics for the Gas-Phase Processes Relevant to Donor-Only Stabilized Cubanes[a] (B3LYP/TZVP Level of Theory)

| | $[DMY]_4 = [MY]_4 + 4D$ | | | $[HMYH]_4 + 4D = [DMY]_4 + 4H_2$ | | | $D\text{-}MH_3 + H_3Y = {}^1/_4[DMY]_4 + 3H_2$ | | |
|---|---|---|---|---|---|---|---|---|---|
| M−Y | $\Delta H°_{298}$ | $\Delta S°_{298}$ | $\Delta G°_{298}$ | $\Delta H°_{298}$ | $\Delta S°_{298}$ | $\Delta G°_{298}$ | $\Delta H°_{298}$ | $\Delta S°_{298}$ | $\Delta G°_{298}$ |
| B−N | 459 | 600 | 280 | 446 | −104 | 477 | 91 | 68 | 70 |
| Al−N | 549 | 531 | 391 | 659 | −49 | 673 | 59 | 67 | 39 |
| Ga−N | 399 | 524 | 243 | 834 | 2.0 | 833 | 186 | 77 | 163 |
| B−P | 352 | 618 | 168 | 78 | −126 | 116 | 117 | 62 | 98 |
| Al−P | 474 | 549 | 310 | −127 | −95 | −98 | −34 | 63 | −53 |
| Ga−P | 331 | 526 | 174 | 1.4 | −51 | 16.5 | −3.0 | 70 | −24 |
| B−As | 368 | 626 | 182 | −6.2 | −129 | 32 | 114 | 61 | 96 |
| Al−As | 444 | 551 | 280 | −238 | −95 | −210 | −65 | 63 | −84 |
| Ga−As | 300 | 532 | 141 | −128 | −51 | −113 | −47 | 71 | −68 |

[a] D = $NH_3$. Standard enthalpies $\Delta H°_{298}$ and standard Gibbs energies $\Delta G°_{298}$ are in kJ $mol^{-1}$, and standard entropies $\Delta S°_{298}$ are in J $mol^{-1}$ $K^{-1}$.

stabilization (Table 4). Nevertheless, partly stabilized cubanes are expected to be very reactive due to easy accessible unprotected M or Y centers. Thus, despite the energetic favorability of their formation, partly "dressed" cubanes are expected to be unstable toward side reactions.

## Conclusions

DA "dressing" is a viable method for stabilization of the "naked" $[MY]_4$ cubanes. The most promising synthetic pathway toward $[DMYA]_4$ compounds is stepwise $H_2$ elimination from $D-MH_3$ and $YH_3-A$. From the thermodynamic point of view, Al-based compounds (Al−N and Al−P systems) are the most promising systems for the experimental studies. Although donor-only stabilization is energetically sufficient for P- and As-containing cubanes, partly stabilized $[DMY]_4$ cubanes are expected to be very reactive because of their easily accessible unprotected donor centers.

By analogy with known $[RMYR']_n$ compounds, where the size of the substituents R and R′ determines the oligomerization degree *n*, it is expected that varying the sizes of the donor and acceptor molecules will allow one to generate a series of $[DMYA]_n$ compounds, including cubane-type tetramers $[DMYA]_4$. These theoretical predictions await experimental realization.

**Acknowledgment.** I am grateful to the Alexander von Humboldt Foundation for partial financial support of this work. The excellent service of the computer cluster of St. Petersburg State University and the MARC computer cluster of Philipps Universität Marburg is gratefully acknowledged.

**Supporting Information Available:** Optimized geometric parameters, predicted harmonic vibrational frequencies, and IR intensities for $[MY]_4$, $[(NH_3)MY]_4$, and $[(NH_3)MY(BH_3)]_4$ cubanes and the total energies of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.