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Structural and Thermodynamic Properties of Group 13 Imidometallanes and Their Heavier Analogues

Alexey Y. Timoshkin*

Inorganic Chemistry Group, Department of Chemistry, St. Petersburg State University, University Pr. 26, Old Peterhof, 198504, Russia

Henry F. Schaefer, III[†]

Center for Computational Chemistry, University of Georgia, Athens, Georgia 30602

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Systematic theoretical studies of the $[XMYH]_n$ inorganic rings and clusters (M = Al, Ga, In; Y = N, P, As; X = H, F, Cl, Br, I; $n = 1–6$) have been carried out using hybrid Hartree–Fock density functional theory. A consistent set of the structural and thermodynamic properties has been obtained. The stability of the MY bond decreases in the order Al > Ga ≥ In; N ≫ P > As. Terminal groups X have a minor influence on the subsequent elimination enthalpies of the clusters. In the case of X = H, hydrogen elimination makes formation of the $[HMYH]_6$ oligomers from MH_3 and YH_3 thermodynamically favorable; while in the case of halide substituents, formation of $[XMYH]_6$ is thermodynamically unfavorable, except for the system with the strongest MY bond (AlN). Substitution of the acidic hydrogen by X is favorable energetically for all $[HMYH]_6$ clusters, but is complicated by the processes of cluster destruction to form the $[X_2MYH_2]_2$ dimers. The high stability of the $[HMNH]_6$ clusters makes them attractive single-source precursors for the production of 13–15 composites.

Introduction

Group 13−15 binary materials (GaAs, GaN, etc.) play important roles in modern microelectronics. They serve as light-emitting diodes, high electron mobility transistors, and advanced ceramic materials. The usual method for their production is chemical vapor deposition (CVD) from organometallic (1) or inorganic (2) precursors.[1]

$$GaMe_3(g) + AsH_3(g) = GaAs(s) + 3CH_4(g) \quad (1)$$

$$AlCl_3(g) + NH_3(g) = AlN(s) + 3HCl(g) \quad (2)$$

Very promising are 13−15 composite materials (alloys), which contain different metal and pnictogen atoms. Such mixed alloys may be in principle produced by codeposition of the different source molecules. For example, $Al_xGa_yIn_{1-x-y}N$ alloy is produced[2] from trimethylgallium (TMG), trimethylaluminum (TMA), trimethylindium (TMI) and ammonia:

$$xAlMe_3 + yGaMe_3 + (1 - x - y)InMe_3 + NH_3 = Al_xGa_yIn_{1-x-y}N + 3CH_4 \quad (3)$$

However, the stoichiometry control of the product formed in reaction 3 is still a challenging task. To achieve stoichiometry control, the exploitation of single-source precursors (SSP) is very promising. Several experimental studies[3−6] suggest that rings and clusters may be formed directly in the gas phase in the course of CVD of binary nitrides:

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* Author to whom correspondence should be addressed. E-mail: alextim@AT11692.spb.edu.

[†] E-mail: hfs@uga.edu.

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$$R_3M + NH_3 = R_3MNH_3 = \underset{\text{“amido” } (m = 2, 3)}{{}^{1}/_{m}[R_2MNH_2]_m} + HR = \underset{\text{“imido” } (n = 2-6)}{{}^{1}/_{n}[RMNH]_n} + 2HR = MN + 3HR \quad (4)$$

Thus, inorganic ring and cluster compounds appear to be natural precursors. There have been both successful[7] and unsuccessful[8] attempts to use ring and cluster compounds as SSP. Experimentally known amido compounds are limited to the monomers, dimers, and trimers only. This small variety obviously limits their use as SSP for the mixed metal alloys, because only 1:1 and 1:2 M:M′ ratios are possible in principle. In contrast, imido compounds $[RMYR']_n$ possess a much greater variety of oligomers. The existence of these compounds in the solid state is well documented.[9−13] The oligomerization degree in such compounds is controlled by the bulkiness of the terminal ligands R,R′: the more bulky ligands result in lower degrees of oligomerization. Imido compounds with $n = 2, 3, 4, 5, 6, 7, 8, 10, 15, 16$ are known experimentally.[9,13] Imido compounds have several advantages compared to amido compounds: they offer a larger variety of M/M′ metal ratios; they possess half as many terminal groups, and, starting from hexamers, they exhibit structures that are very similar to the solid-state structures of 13−15 materials. With the goal to use imido compounds and their heavier analogues $[RMYR']_n$ as SSP, knowledge of their gas-phase stability becomes essential. Despite extensive studies in the condensed phase, the gas-phase chemistry of these compounds is not at all well documented. Previous theoretical studies[14−16] of the group 13 pnictidometallanes were mostly concentrated on the $[HMYH]_3$ rings, which are inorganic analogues of benzene. The potential of cyclic dimeric amido compounds as SSP have been explored theoretically by Ni, York, Bartolotti, Wells, and Yang.[17] Other investigations are limited to case studies of AlN,[18−20] GaN,[21−23] and AlP.[24] Dimerization of inorganic benzenes $[HMYH]_3$ (M = B, Al, Ga; Y = N, P, As) was considered in a recent study.[25] The chemistry of boron analogues will not be discussed in the present report. The high stability of the aromatic borazine $[HBNH]_3$ and its derivatives makes formation of the cluster species in boron-containing systems highly unfavorable, as indicated by the high endothermicity of the borazine dimerization.[25] Boron-containing alloys are less important for practical applications due to the large difference in the lattice parameters of binary compounds of boron and its heavier analogues.

The role of the partners MY and the substituents (terminal groups) X in the formation of $[XMYH]_n$ is not fully understood. The thermodynamic properties and stabilities of such complexes in the gas phase are unknown. In the present report results of systematic computational investigations of $[XMYH]_n$ inorganic rings and clusters (M = Al, Ga, In; Y = N, P, As; X = H, F, Cl, Br, I; $n = 1-6$) are summarized. Some of our preliminary results on the stability of dimeric[26] and trimeric/tetrameric[27] compounds have appeared in conference proceedings. The present report makes it possible to discuss trends with respect to cluster size (oligomerization degree n), and the influence of the metal, pnictogen atoms, and terminal groups X on the structures and stability of clusters.

Computational Details

Density functional theory in the form of the hybrid B3LYP functional[28] was used together with the basis sets of Hay and Wadt,[29] augmented by d and p polarization functions (denoted later as LANL2DZ(d,p)). The following orbital exponents were used: p exponent for H (1.0) and d exponents for Al (0.4), Ga (0.16), In (0.16), N (0.8), P (0.5), As (0.25), F (0.8), Cl (0.56), Br (0.25), and I (0.15). The Gaussian 94 suite of programs[30] was used throughout. All structures were fully optimized with subsequent vibrational analyses and correspond to minima on the potential energy surfaces (PES). The Gibbs energy at a given temperature was evaluated using standard values of the enthalpy and entropy according to the equation $\Delta G^\circ_T = \Delta H^\circ_{298} - T\Delta S^\circ_{298}$.

As shown previously, the B3LYP/LANL2DZ(d,p) method gives a good description of the gas-phase thermochemistry of the X_3MYH_3 donor−acceptor compounds.[31] In the recent case study of ClGaNH oligomers,[22] the mean difference between the pVDZ

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Table 1. Comparison of the Energies ΔE_0 (kJ mol^{-1}) ($T = 0$ K) of the Selected Reactions Predicted at Different Levels of Theory

	level of theory		
process	B3LYP/ LANL2DZ(d,p)^a	CCSD(T)/ cc-pVTZ^a	CCSD(T)/ cc-pVTZ^b
$H_3AlNH_3 = AlH_3 + NH_3$	−122.9	−129.4	−129.4
$H_3AlNH_3 = HAlNH + 2H_2$	321.4	331.1	331.0
$HAlNH = {}^1/_2[HAlNH]_2$	−287.9	−297.2	−296.8
${}^1/_2[HAlNH]_2 = {}^1/_3[HAlNH]_3$	−59.4	−60.7	−60.8
${}^1/_3[HAlNH]_3 = {}^1/_4[HAlNH]_4$	−58.4	−66.5	
$H_3AlPH_3 = AlH_3 + PH_3$	−52.7	−61.2	−61.4
$H_3AlPH_3 = HAlPH + 2H_2$	198.5	182.3	182.0
$HAlPH = {}^1/_2[HAlPH]_2$	−171.5	−181.1	−180.6
${}^1/_2[HAlPH]_2 = {}^1/_3[HAlPH]_3$	−34.4	−35.8	
${}^1/_3[HAlPH]_3 = {}^1/_4[HAlPH]_4$	−28.8	−39.3	

[a] At B3LYP/LANL2DZ(d,p) optimized geometries. [b] At CCSD(T)/cc-pVTZ optimized geometries.

and LANL2DZ(d,p) basis sets is 20 kJ mol^{-1} and 5 J mol^{-1} K^{-1} in standard enthalpies and entropies, respectively. In order to further test the reliability of the B3LYP/LANL2DZ(d,p) level of theory (as one of the referees suggested), high-level ab initio computations have been performed for the selected molecules ($M = Al$, $Y = N$, P). Single-point energy computations at B3LYP/LANL2DZ(d,p) optimized geometries have been performed at the CCSD(T) level of theory[32] with the cc-pVTZ basis set[33] as implemented in the MOLPRO package.[34] In the case of small molecules, geometry optimizations at the CCSD(T)/cc-pVTZ level of theory have been also performed. Due to the high memory requirements, even the smallest hexamer cluster $[HAlNH]_6$ (552 basis functions) could not be treated at the CCSD(T)/cc-pVTZ level of theory, and therefore only oligomers with *n* up to four have been considered. There is satisfactory agreement between the B3LYP and CCSD(T) results (Table 1). The mean difference for the reaction energies is 7.2 kJ mol^{-1} (maximal 16.5 kJ mol^{-1}). Note that the difference between the single-point CCSD(T)/cc-pVTZ energies at the B3LYP/LANL2DZ(d,p) geometries and at CCSD(T)/cc-pVTZ optimized geometries is very small ($\leq$0.5 kJ mol^{-1}), suggesting that the B3LYP/LANL2DZ(d,p) geometries are reliable.

Results and Discussion

I. Structures of Compounds. A. Structural Features. Figure 1 presents general structures for the $[XMYH]_n$ compounds ($n = 1-6$) studied in the present work. The most important structural parameters are summarized in the Supporting Information (Tables 1S−6S). Vibrational frequencies and IR intensities for all compounds studied are also provided (Tables 7S−12S). Later in the text we will briefly discuss important individual structural features of the oligomer compounds.

Monomer species [XMYH] have been studied only as starting points for the oligomerization reactions. Only singlet electronic states have been considered here. Highly unsaturated metal and pnictogen centers preclude the existence of these compounds in the gas phase, due to highly favorable oligomerization reactions.

Dimers $[XMYH]_2$ are produced by the head-to tail dimerization of the XMYH monomers. They are planar in the case of $Y = N$ (D_{2h} point group, Figure 1b), and adopt pyramidal geometries around the pnictogen centers in the cases $Y = P$, As. In the latter cases two types of isomers are possible: (a) C_{2v} symmetric *cis* (Y−H groups are pointing in the same direction with respect to the M_2Y_2 ring, Figure 1d); and (b) C_{2h} symmetric *trans*, in which the Y−H groups are orientated differently with respect to the M_2Y_2 core (Figure 1c). Both isomers are minima on the PES. For all investigated compounds the C_{2v} isomer is the most stable; however, the mean energy difference between C_{2v} and C_{2h} structures is only 5 kJ mol^{-1} (at most 15 kJ mol^{-1}). In several cases we encountered a situation where the C_{2h} structure of the dimer is not a minimum on the PES. Further lowering of the symmetry (to C_s point group) resulted in the nonplanar (butterfly distorted) ring with inequivalent M−Y distances. The relative energies of these structures were always higher compared to the C_{2v} symmetric isomer. Therefore, it is concluded that, among the cyclic structures with the M_2Y_2 core, the C_{2v} symmetric *cis*-isomers are the global minima on PES.

Trimers $[XMYH]_3$. In agreement with previous theoretical[14,15,25] results the nitrogen-containing inorganic benzenes are planar (D_{3h} point group, Figure 1e) while the P, As compounds adopt pyramidal geometries. In the present work we have considered only C_{3v} symmetric *cis*-isomers in which all the M−X and Y−H bonds are ordered in the same manner with respect to the M_3Y_3 core (Figure 1f), because these isomers were found to be more stable in recent studies of inorganic benzenes.[25] It should be noted that the open structure of the trimers (planar in the case of N, C_{3v} cisoid for P, As) kinetically favors their dimerization. In fact, only four trimer compounds with bulky substituents R,R′ have been synthesized so far, although many more hexamers are experimentally known.

Tetramers $[XMYH]_4$. These T_d symmetric species (Figure 1g) are the simplest clusters in which both metal and pnictogen centers have coordination number 4. As expected, increasing the coordination number elongates the M−Y distances.

Pentamers $[XMYH]_5$ can be formally obtained by adding one XMYH unit to the tetramer. They adopt the C_s point group for $Y = N$ (Figure 1h), but pyramidalization of the pnictogen centers for $Y = P$, As leads to asymmetric molecules (Figure 1i). Pentamers have one M and one Y center with low coordination number 3 and are expected to be less stable compared to species with coordination number 4. Initial results on hydrogen-substituted species (Table 13S) indeed show that their conversion into hexamers is thermodynamically favorable. Therefore, halide substituted pentamers will not be considered in the present report.

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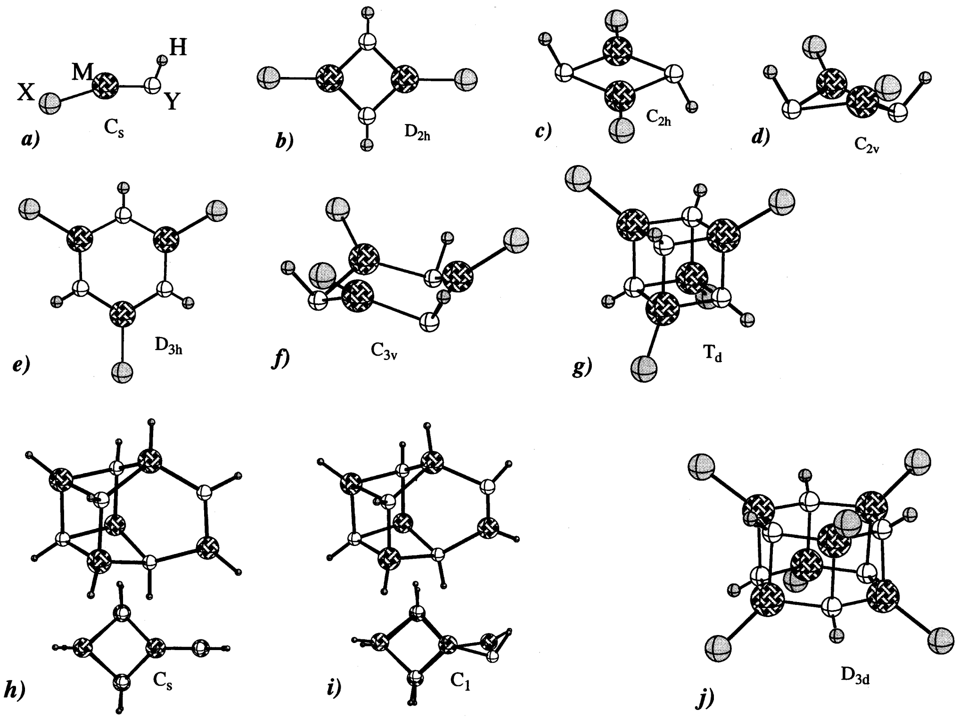

Figure 1. Structures of the investigated compounds: (a) XMYH monomers; $[XMYH]_2$ dimers of D_{2h}, (b), C_{2h} (c), and C_{2v} (d) symmetry; $[XMYH]_3$ trimers of D_{3h} (e) and C_{3v} (f) symmetry; $[XMYH]_4$ tetramers (g); $[HMYH]_5$ pentamers of C_s (h) and C_1 (i) symmetry; $[XMYH]_6$ hexamers (j).

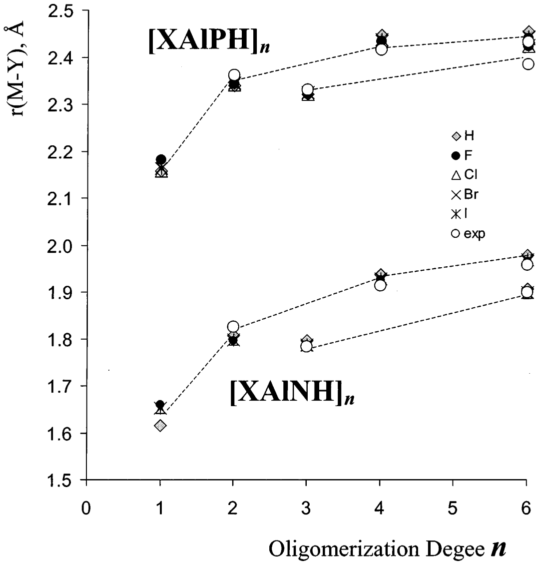

Figure 2. Trends in the M−Y distance, r(M−Y), Å, as a function of the oligomerization degree n for the $[XAlYH]_n$ (Y = N, P) species. Predicted results are from the B3LYP/LANL2DZ(d,p) level of theory. Experimental bond distances are average values from all experimentally known compounds $[RAlYR']_n$ of the same n. Lines are drawn only to guide the eye.

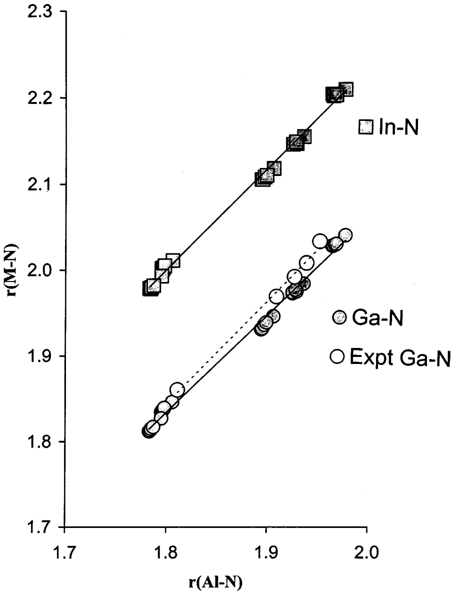

Figure 3. Relationships between the theoretical Al−N and Ga−N/In−N bond distances for oligomer compounds. Experimental values are also shown for comparison. All distances are in Å.

Hexamer $[XMYH]_6$ compounds are formed by the fusion of two trimers. They are the largest species studied in the present work (for all X). These species possess D_{3d} point group (Figure 1j).

B. Trends in Structural Parameters. Figure 2 presents in a schematic way trends in the Al−N and Al−P bond distances as a function of the oligomerization degree n. Mean experimental values of the Al−N and Al−P bond distances are also shown in Figure 2 for comparison. Trends for the all other $[XMYH]_n$ species are qualitatively the same. In general, the MY bond distance increases with the increase of the oligomerization degree n, but this change is not monotonic. The MY bonds in the trimers are shorter compared to those in the dimers and tetramers. This may be rationalized in terms of the strain of the four-membered ring. It seems likely that the large charge separation and shorter M···M and Y···Y distances in the dimers are responsible for such high reorganization energies. As a result, the M−Y distances in the trimers are 0.01−0.02 Å shorter compared to those in the dimers. The M−Y distances for the four-membered rings in hexamers are also always longer compared to those in the six-membered rings. Note that if the

Table 2. Relative Energies of the Planar Structures of H_2MYH_2 and $[HMYH]_{2,3,5}$ Relative to the Corresponding Minima on the PES in kJ mol^{-1} (B3LYP/LANL2DZ(d,p) Level of Theory) and Inversion Barriers of YH_3

	H_2MYH_2			$[HMYH]_2$[a]			$[HMYH]_3$[b]			$[HMYH]_5$[c]			
	Al	Ga	In	Al	Ga	In	Al	Ga	In	Al	Ga	In	YH_3[d]
N	0	0	0	0	0	0	0	0	0	0	0	0	29.6
P	38.6	46.9	52.2	73.2	91.0	85.7	49.0	81.4	93.5	17.1	25.6	30.8	148.8
As	56.2	62.7	68.1	108.2	122.7	119.9	96.3	119.3	136.0	30.9	37.6	64.1	192.4

[a] Energy of the D_{2h} symmetric structure compared to C_{2v} symmetric. [b] Energy of the D_{3h} symmetric structure compared to C_{3v} symmetric. [c] Energy of the C_s symmetric structure compared to C_1 symmetric. [d] B3LYP/6-31G* level of theory, ref 15.

distances in the four- and six-membered-ring compounds are considered separately, the trends (**1**) < (**2**) < (**4**) < (**6**) and (**3**) < (**6**) are obtained for the four- and six-membered cycles, respectively (Figure 2). As may be seen from Figure 2, the Al−N and Al−P distances exhibit a similar trend with the increase of the oligomerization degree. Substitution of Al by Ga and In leads to the same picture. Moreover, there is a good correlation between Al−N bond distances and Ga−N (In−N) distances (Figure 3) for cyclic and cage species:

$$r(\text{Ga}-\text{N}) = 1.1313r(\text{Al}-\text{N}) - 0.2025; \quad R^2 = 0.995$$

$$r(\text{In}-\text{N}) = 1.1754r(\text{Al}-\text{N}) - 0.1153; \quad R^2 = 0.996$$

Although the experimental distances are somewhat higher compared to the predicted ones, a good correlation also holds for the experimental Al−N and Ga−N bond distances in compounds bearing identical terminal groups (Figure 3):

$$r(\text{Ga}-\text{N})_{\text{exp}} = 1.1875r(\text{Al}-\text{N})_{\text{exp}} - 0.2928; \quad R^2 = 0.994$$

(Such pairs are available for the tetramers $[MeMN\text{-}t\text{-}Bu]_4$ (M = Al[35a] and M = Ga[35b]) and $[MeMN(C_6F_5)]_4$ (M = Al[36a] and M = Ga[36b]) and the hexamer $[MeMN(4\text{-}C_6H_4F]_6$ for M = Al, Ga.[37] For dimeric cycles, values of M−N bond distances in $Cp^*\{(Me_3Si)_2N\}AlN(\mu\text{-}AlCp^*)$ $(\mu\text{-}Al\{N(SiMe_3)_2\})NAlCp_2^*$ ($Cp^* = \eta^1\text{-}C_5Me_5$)[38] and $[\eta^1\text{-}C_5Me_5\text{-}GaNXyl]_2$[39] have been chosen.)

Note that the Ga−N bond is always longer compared to Al−N. This fact reflects the weaker bonding in the case of Ga, which has also been found for the Cl−M−N−H systems.[22] Correlation between the Al−Y and Ga−Y/In−Y bond distances is also observed for Y = P, As (see Supporting Information figure), but in this case the correlation is less perfect, reflecting the fact that that the nature of M plays some role in the pyramidalization of the Y center. Since the theoretically observed trends are the same for all Y with different X, we conclude that the MY bonds exhibit similar trends for all substituents.

C. Pyramidalization of the Pnictogen Centers. As shown above, the P and As centers adopt a pyramidal structure in compounds where they have coordination number 3. The results obtained in the present study allow us to compare the pyramidalization energies in different coordination environments of the pnictogen center: from simple YH_3 to X_2MYH_2 and $[XMYH]_{2,3,5}$ compounds. Planar nirogen and pyramidal P, As centers have been predicted earlier for X_2MYH_2,[40,41] $[XMYH]_2$,[26] and $[HMYH]_3$[15,25,27] compounds. The distortion of the P, As centers (pyramidalization) was attributed by Jemmis and Kiran[15] to the much higher inversion barriers of PH_3 and AsH_3 (149 and 192 kJ mol^{-1}, respectively) compared to only 30 kJ mol^{-1} for NH_3.

Let us carefully consider the case of X = H. Relative energies of the planar structures with respect to the pyramidal are given in Table 2. As may be seen, increasing the number of the metal centers (connected to Y) significantly decreases the barrier to “planarization”. Thus, all species with Y = N are planar. The relationship between the number of metal atoms bonded to Y and the “planarization” energy E (per one Y center) is shown in Figure 4. The mean values are plotted in Figure 4, and the error bars represent the range of energies for the different metal atoms. In general, increasing the number of metal centers bonded to Y decreases the pyramidalization energy. Thus, nitrogen, with its small inversion energy in NH_3, becomes planar in all compounds when H is substituted by the metal. For Y = P, As stabilization is not sufficient to favor planar structures, but significantly (by 100−150 kJ mol^{-1}) lowers the barrier for “planarization”.

II. Thermodynamics. A. Subsequent Oligomerization Enthalpies. Subsequent oligomerization enthalpies are presented in Table 3. Note that for the nitrogen- and aluminum-containing molecules all oligomerization enthalpies are negative, indicating the high favorability of the oligomerization processes. Note also that the change of X leads to small changes in oligomerization enthalpies. The enthalpy of the dimer−trimer reorganization is interesting, since in this reaction all bonds are formally preserved and all atoms have similar coordination environments (planar for Y = N, pyramidal for Y = P, As). The reorganization energies

$$^1/_2[\text{XMYH}]_2 = {}^1/_3[\text{XMYH}]_3$$

are strongly exothermic (−53−72 kJ mol^{-1} for Y = N; −33−39 kJ mol^{-1} for Y = P; −29−34 kJ mol^{-1} for Y = As), suggesting high ring strain in the four-membered cycles.

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Table 3. Standard Enthalpies (kJ mol^{-1}) of Subsequent Oligomerization Reactions, Reported per Mole of Monomer: $^{1}/_{n-1}[XMYH]_{n-1} = {}^{1}/_{n}[XMYH]_{n}$[a]

		Y = N				Y = P				Y = As			
M	X	$n = 2$	$n = 3$	$n = 4$	$n = 6^{b}$	$n = 2$	$n = 3$	$n = 4$	$n = 6^{b}$	$n = 2$	$n = 3$	$n = 4$	$n = 6^{b}$
Al	H	−281.7	−58.1	−57.5	−23.4	−165.5	−32.8	−28.5	−21.3	−151.6	−29.4	−15.0	−20.4
						−165^{c}							
	F	−320.3	−64.6	−63.3	−28.9	−206.9	−34.5	−24.9	−23.1	−210.4	−30.5	−8.2	−22.3
	Cl	−311.9	−63.6	−61.0	−26.9	−172.9	−33.6	−25.6	−22.1	−178.5	−29.6	−9.5	−21.3
		−301^{d}	−63^{d}	−57^{d}	−26^{d}								
	Br	−305.0	−62.5	−59.1	−25.9	−167.8	−33.0	−24.2	−21.9	−169.5	−29.1	−8.5	−21.1
	I	−298.6	−61.7	−57.7	−24.8	−163.2	−32.7	−23.8	−21.7	−155.3	−28.8	−8.5	−20.9
Ga	H	−227.5	−60.6	−37.6	−21.3	−165.8	−34.9	−9.6	−19.2	−168.2	−31.8	0.4	−19.5
		−207^{e}	−59^{e}	−41^{e}	−20^{e}								
	CH_3	−201^{e}	−55^{e}	−42^{e}	−19^{e}								
	F	−247.1	−71.5	−38.0	−29.3	−154.6	−38.8	1.6	−21.4	−132.1	−34.3	15.4	−21.7
	Cl	−245.6	−69.1	−36.8	−26.7	−136.5	−36.9	−0.2	−20.4	−129.4	−32.2	12.6	−20.8
		−221^{f}	−68^{f}	−42^{f}	−26^{f}								
	Br	−240.7	−67.7	−36.1	−25.6	−134.5	−36.0	−0.2	−20.1	−127.1	−31.6	12.3	−20.6
	I	−236.8	−65.8	−36.0	−24.1	−135.2	−34.9	−1.0	−19.7	−124.4	−30.6	11.0	−20.2
In	H	−212.8	−52.5	−57.2	−17.8	−150.1	−34.7	−20.8	−16.4	−155.4	−31.6	−7.5	−17.1
	F	−217.6	−63.9	−57.7	−25.6	−156.6	−38.2	−9.5	−19.6	−161.9	−33.1	6.7	−19.7
	Cl	−220.3	−63.4	−56.0	−24.2	−132.8	−37.5	−9.9	−18.9	−140.2	−32.1	5.8	−19.2
	Br	−217.4	−61.8	−55.0	−23.1	−131.2	−36.4	−9.5	−18.6	−132.2	−31.3	5.7	−19.0
	I	−215.2	−60.3	−54.2	−22.1	−127.1	−35.5	−9.7	−18.3	−124.8	−30.6	5.1	−18.7

[a] All results are at the B3LYP/LANL2DY(d,p) level of theory, if not otherwise indicated. [b] Values are given for the reaction $^{1}/_{4}[XMYH]_4 = {}^{1}/_{6}[XMYH]_6$. [c] DZP/CCSD level of theory, obtained from results given in ref 24. [d] B3LYP/DZP level of theory, ref 18. [e] B3LYP/pVDZ level of theory, ref 21. [f] B3LYP/pVDZ level of theory, ref 22.

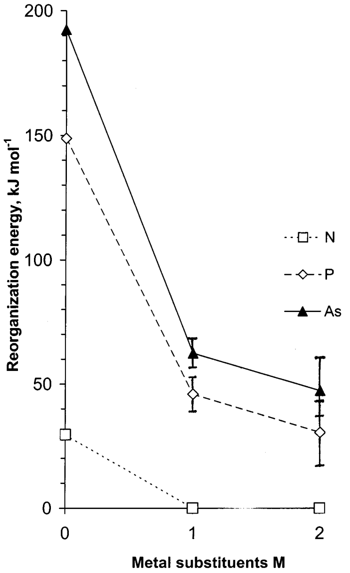

Figure 4. Mean values of the reorganization energy of YR_3 versus the number of metal substituents M. Error bars represent the range of values of the reorganization energy for different metal centers.

For Y = As the trimer−tetramer reorganization enthalpy is endothermic (unfavorable) in the case of Ga, In compounds with halide substituents. The value for X = H is only slightly favorable in the case of In. Thus, a substantially lower stability of the tetramer species in the case of As is expected. This conclusion dovetails with available experimental results: among the structurally characterized tetramers (more than 20) As-containing cubes are still unknown. Attempts at their synthesis resulted in hexamer species, which are more stable thermodynamically.[42]

B. Formation of Oligomers from MX_3 and YH_3. The thermodynamic parameters for formation of the hexamer clusters from MX_3 and YH_3 are given in Table 4. Values obtained with full-electron basis sets are also shown for comparison. For X = Cl both the reaction enthalpies and entropies predicted with the DZP (all electron) and LANL2DZ(d,p) basis sets are in good agreement, whereas in the case X = H the difference between standard enthalpies of reactions is more pronounced. The Gibbs energies of two processes, namely, dissociation of the adduct $X_3MYH_3 = X_3M + YH_3$ (denoted later as diss) and formation of hexamer compound $X_3MYH_3 = {}^{1}/_{6}[XMYH]_6 + 2HX$ (denoted as elim+hex) are compared in Figure 5 a and Figure 5b, for the temperatures 500 and 1000 K, respectively. Only for the hydrogen-containing compounds is formation of the hexamer species in the gas phase favorable thermodynamically ($\Delta G^{\mathrm{elim+hex}} < 0$). These energies are also smaller compared to dissociation of the adduct. Note the difference between the nitrogen and P, As-containing compounds: P, As-containing adducts are thermodynamically unstable already at 500 K ($\Delta G^{\mathrm{diss}}_{500} < 0$), while the N-containing adducts are stable ($\Delta G^{\mathrm{diss}}_{500} > 0$). Thus, cleavage of the M−Y bonds proceeds easily for the P, As-containing adducts. For halide substituents elimination reactions are endothermic and even more unfavorable compared to dissociation of the adduct (the exception is the I−Al−N−H system, where these energies are close). Therefore, in contrast to the hydrides, for halide substituents the hexamer species are not the thermodynamically most stable products in the gas phase.

The present results allow us to compare the energetics of the elimination of the first and the second HX molecules from the donor−acceptor complexes X_3MYH_3. Results are shown in Figure 6. Gibbs energies at 1000 K have been compared for the HX elimination reactions with formation of the dimeric amido $[X_2MYH_2]_2$ and imido $[XMYH]_2$ rings.

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(42) Synthesis of $[EtInAsSi(iPr)_3]_4$ has been reported recently (von Hänisch, C.; Rolli, B. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2255), but no X-ray crystal structure is available.

Table 4. Thermodynamic Characteristics of Selected Gas Phase Reactions Predicted at the B3LYP/LANL2DZ(d,p) Level of Theory (Standard Enthalpies in kJ mol^{-1}, Standard Entropies in J mol^{-1} K^{-1}

			$MX_3 + YH_3 = {}^1/_6[XMYH]_6 + 2HX$		${}^1/_6[XMYH]_6 + HX = {}^1/_2[X_2MYH_2]_2$		${}^1/_6[XMYH]_6 = MX + {}^1/_mY_m + {}^1/_2H_2$[a]	
Y	M	X	ΔH°_{298}	ΔS°_{298}	ΔH°_{298}	ΔS°_{298}	ΔH°_{298}	ΔS°_{298}
N	Al	H	−259.1	−63.3	53.5	−47.2	449.8	272.8
		F	100.8	−33.4	−153.4	−69.2	383.9	278.3
		Cl	18.4 (27.2[b])	−22.2 (−24.2[b])	−105.2 (−106.7[b])	−70.6 (−68.8[b])	386.1	279.1
		Br	10.0	−22.8	−96.3	−70.2	376.8	279.0
		I	−15.7	−23.9	−78.8	−69.7	372.5	278.8
	Ga	H	−171.0 (−137.1[d])	−62.7 (−62.2[d])	16.7 (−7.5[c])	−47.4 (−47.6[c])	317.8	273.2
		F	71.5	−23.8	−131.2	−68.8	233.6	277.9
		Cl	39.3 (56.9[d])	−42.6 (−22.0[d])	−108.3 (−116.6[d])	−69.1 (−70.2[d])	235.2	298.7
		Br	52.8	−22.7	−108.7	−69.2	227.7	278.6
		I	49.0	−23.9	−100.6	−68.5	226.5	278.4
	In	H	−147.7	−61.2	5.6	−46.1	234.5	269.4
		F	88.0	−24.1	−133.2	−65.0	155.3	272.7
		Cl	70.4	−22.8	−122.1	−65.9	152.1	273.2
		Br	98.7	−22.1	−131.2	−66.2	147.6	272.9
		I	102.7	−23.3	−128.2	−65.1	146.5	272.6
P	Al	H	−125.2	−55.7	30.5	−39.2	294.1	221.8
		F	252.1	−25.0	−167.6	−66.6	210.8	226.4
		Cl	166.4	−14.1	−119.9	−67.1	216.3	227.6
		Br	154.8	−14.4	−112.1	−67.0	210.2	227.2
		I	125.5	−15.4	−95.7	−68.2	209.5	226.9
	Ga	H	−98.6	−54.9	21.4	−41.1	223.6	222.0
		F	158.9	−14.5	−115.1	−65.7	124.4	225.2
		Cl	125.1	−13.9	−94.0	−66.6	127.6	226.6
		Br	133.2	−13.6	−95.6	−66.3	125.5	226.1
		I	126.7	−14.8	−89.2	−66.9	127.0	225.9
	In	H	−117.6	−53.2	34.1	−43.0	182.6	218.0
		F	127.1	−15.1	−95.9	−63.0	94.4	220.3
		Cl	109.4	−14.2	−85.9	−64.3	91.3	221.2
		Br	135.6	−13.4	−95.8	−64.9	88.9	220.8
		I	138.2	−14.4	−94.0	−64.2	89.2	220.3
As	Al	H	−127.1	−54.2	39.1	−40.0	253.7	219.6
		F	251.5	−22.9	−158.5	−67.0	169.1	223.7
		Cl	165.7	−12.2	−110.8	−68.9	174.8	225.1
		Br	153.5	−12.6	−102.9	−68.1	169.2	224.7
		I	123.8	−13.7	−86.5	−68.9	168.9	224.5
	Ga	H	−108.4	−53.9	34.0	−42.3	191.2	220.3
		F	150.5	−12.8	−101.4	−65.6	90.6	222.8
		Cl	115.9	−12.6	−80.2	−67.0	94.6	224.6
		Br	123.6	−12.4	−81.9	−66.6	92.9	224.3
		I	116.3	−13.6	−75.6	−67.2	95.1	224.0
	In	H	−135.1	−51.8	49.8	−43.1	157.9	215.9
		F	110.8	−12.7	−78.8	−62.4	68.4	217.2
		Cl	92.0	−12.3	−69.1	−64.3	66.5	218.7
		Br	118.1	−11.6	−79.2	−64.9	64.1	218.3
		I	120.1	−12.7	−77.5	−64.7	65.0	217.9

[a] For Y = N, $m = 2$; for Y = P, As $m = 4$. [b] B3LYP/DZP level of theory, ref 18. [c] B3LYP/pVDZ level of theory, ref 21. [d] B3LYP/pVDZ level of theory, ref 22.

There is a good correlation between the Gibbs energies of these two reactions with coefficients close to 2. Elimination reactions are exothermic for X = H, while for halide substituents they are endothermic. Elimination in the case of Y = N is the most endothermic, reflecting the higher stability of N−H bonds compared to P−H and As−H.

Data in Table 4 show that, for the case X = H, formation of hexamers from MH_3 and YH_3 is favored energetically but disfavored by entropy. Table 5 presents those temperatures at which the equilibrium constant of the equation $MH_3 + YH_3 = {}^1/_6[HMYH]_6 + 2H_2$ equals 1. It can be seen that generation of the hexamer $[HMYH]_6$ clusters is favorable up to very high (≥1800 K) temperatures. The high stability of the Al−N-bonded species makes formation of hexamer species in the gas phase exothermic for X = I and only slightly endothermic for X = Cl, Br (Table 4). Experimental estimations of molecular weights of species responsible for growth of AlN nanoparticles from $AlCl_3$ and NH_3 (450 and 460 amu at 973 and 1023 K, respectively)[3b] are in good agreement with the molecular weight of $[ClAlNH]_6$ hexamer (465 amu).

C. Thermodynamics of Substitution Processes and Cage Degradation Reactions. The high thermodynamic favorability of the formation of hydrogen-containing clusters makes them promising starting points for the generation of other clusters by substitution reactions. In fact, substitution of the hydrogen atoms in $[HMYR]_n$ is a well-known pathway for the condensed-phase synthesis of the substituted imidogallanes.[35a,43−45] HCl, $HgCl_2$, and $TiCl_4$ were used to

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(43) Del Piero, G.; Perego, G.; Cucinella, S.; Cesari, M. C.; Mazzei, A. *J. Organomet. Chem.* **1977**, *136*, 13.

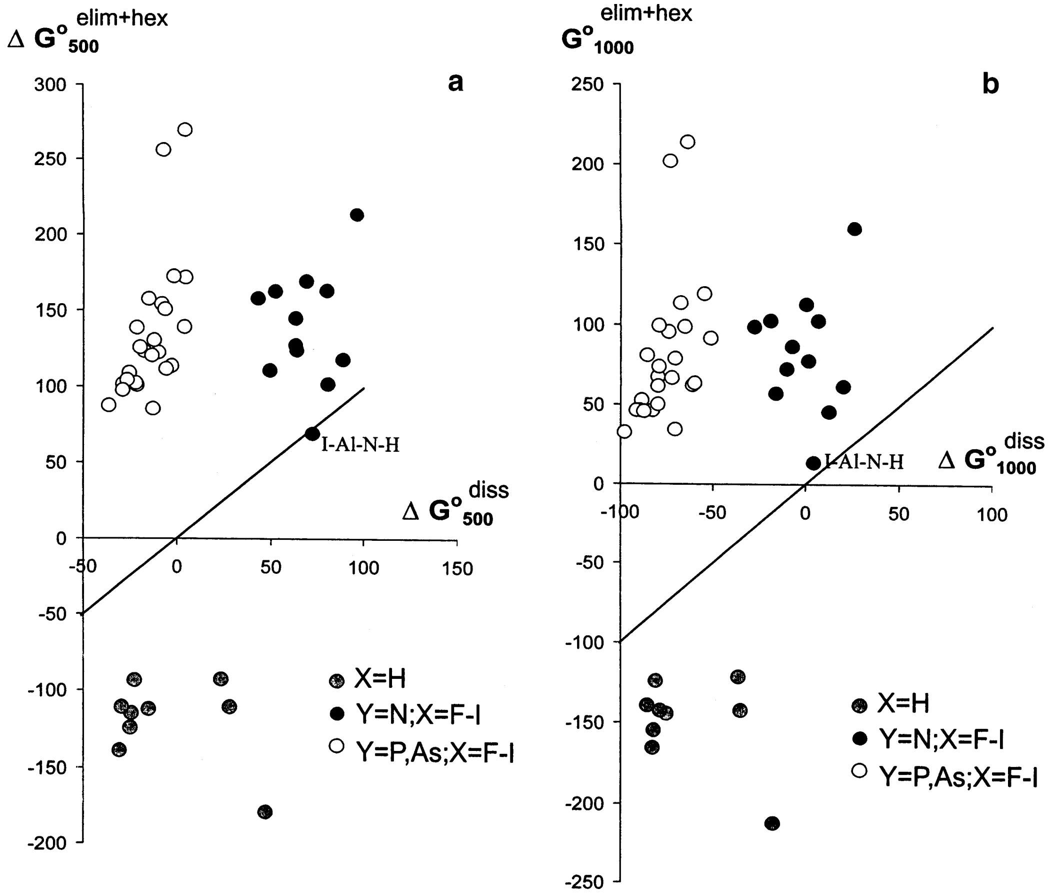

Figure 5. Relationship between Gibbs energies (kJ mol^{-1}) at 500 K (a) and 1000 K (b) for dissociation of the donor−acceptor complexes $X_3MYH_3 = MX_3 + YH_3$ (diss) and HX elimination with formation of the hexamer species: $X_3MYH_3 = {}^1/_6[XMYH]_6 + 2HX$ (elim+hex).

obtain partially or fully chlorinated poly(*N*-alkyliminoalanes);[45] for example, the

$$[HAlNR]_n + nHCl \xrightarrow{Et_2O} [ClAlNR]_n + nH_2$$

reaction was chosen as a model for the substitution processes.

$$^1/_6[HMYH]_6 + HX = {}^1/_6[XMYH]_6 + H_2 \qquad (5)$$

This reaction is exothermic for X = F−I, with enthalpies ranging from −104 kJ mol^{-1} for $[IGaPH]_6$ to −200 kJ mol^{-1} for $[FAlNH]_6$ (Table 6). The entropy factor slightly disfavors this reaction, with $\Delta S°_{298}$ ranging from −17.5 to − 22.5 J mol^{-1} K^{-1}. Therefore, it may be concluded that, in the reaction of hydride clusters with hydrogen halides, formation of the halide-substituted species is thermodynamically favorable. This follows from the higher metal−halogen bond energies compared to the analogous metal−hydrogen systems. Thus, substitution of H in simple MH species is also very favorable thermodynamically. Predicted thermodynamic parameters for the simple reaction $MH + HX = MX + H_2$ may be compared with experimental data, because for all gaseous MX and MH species standard enthalpies of formation are known experimentally.[46] Comparison (Table 7) shows that the B3LYP/LANL2DZ(d,p) method performs very well for these reaction entropies. For the standard enthalpies, there is very good agreement for X = Cl, Br; enthalpies for X = F are underestimated and for X = I are overestimated.

A serious drawback to the substitution reactions is the instability of the imido compounds with respect to the cage degradation reactions. Thus, only five hydrogen atoms are substituted easily in $[HAlNR]_6$ without cage degradation.[45] Attempts to effect the full substitution resulted not only in the expected product $[ClAlNR]_6$ but also in mixtures of the hexameric polyiminoalanes with different degrees of chlorination, together with the chlorinated tetramers and pentamers, and more simple species as $[Cl_2AlNHR]_2$ due to degradation reactions.[45] An excess of the hydrogen halides results in full degradation of the imido compounds:

$$^1/_n[HMYH]_n + 2HX = {}^1/_2[X_2MYH_2]_2 + H_2 \qquad (6)$$

This reaction may be considered as a two-step process: first the exothermic substitution to the corresponding $^1/_n[XMYH]_n$

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(44) Cucinella, S., Salvatori, T.; Busetto, C.; Cesari, M. *J. Organomet. Chem.* **1976**, *121*, 137.

(45) Cucinella, S., Salvatori, T.; Busetto, C.; Mazzei, A. *J. Organomet. Chem.* **1976**, *108*, 13.

(46) Electronic database *Thermal Constants of Substances*, version 28.05.2003; Yungman, V. S., Ed.; http://www.chem.msu.su/cgi-bin/tkv.pl?show=welcome.html, accessed August 2003.

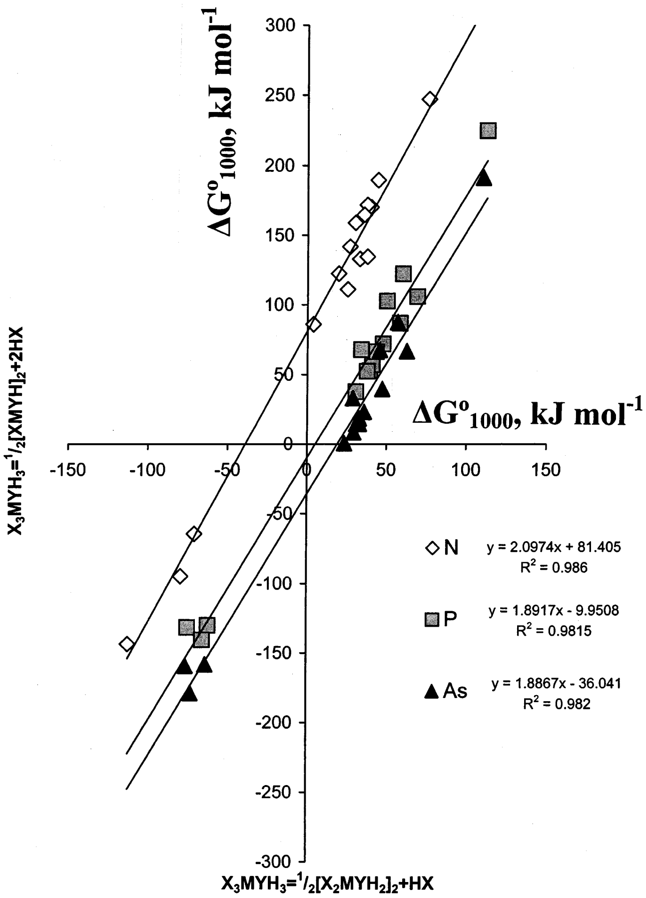

Figure 6. Relationship between the Gibbs energies at 1000 K for elimination of 1 and 2 mol of HX from the donor−acceptor complexes: Abscissa: $X_3MYH_3 = {}^1/_2[X_2MYH_2]_2 + HX$. Ordinate: $X_3MYH_3 = {}^1/_2[XMYH]_2 + 2HX$.

Table 5. Values of the Temperature (K) at Which the Equilibrium Constant for the Corresponding Process Equals 1 (B3LYP/LANL2DZ-(d,p) Level of Theory)

	$MH_3 + YH_3 = {}^1/_6[HMYH]_6 + 2H_2$			${}^1/_6[HMYH]_6 = MH + {}^1/_mY_m + {}^1/_2H_2$[a]		
	M = Al	M = Ga	M = In	M = Al	M = Ga	M = In
Y = N	4090	2730	2410	1650	1160	870
Y = P	2250	1800	2210	1330	1010	840
Y = As	2350	2010	2610	1160	870	730

[a] For Y = N, $m = 2$; for Y = P, As $m = 4$.

Table 6. Thermodynamic Characteristics of the Substitution Reactions ${}^1/_6[HMYH]_6 + HX = H_2 + {}^1/_6[XMYH]_6$ Predicted at the B3LYP/LANL2DZ(d,p) Level of Theory (Standard Enthalpies and Gibbs Energies in kJ mol^{-1}, Standard Entropies in J mol^{-1} K^{-1})

		Y = N		Y = P		Y = As	
M	X	$\Delta H°_{298}$	$\Delta S°_{298}$	$\Delta H°_{298}$	$\Delta S°_{298}$	$\Delta H°_{298}$	$\Delta S°_{298}$
Al	F	−199.8	−21.6	−182.5	−20.8	−181.1	−20.3
	Cl	−153.4	−22.5	−139.4	−22.0	−138.2	−21.6
	Br	−142.5	−22.2	−131.6	−21.5	−131.0	−21.2
	I	−124.3	−21.6	−117.0	−20.8	−116.8	−20.5
Ga	F	−136.8	−20.5	−121.9	−19.0	−120.4	−18.3
	Cl	−118.0	−21.2	−106.5	−20.2	−105.9	−19.8
	Br	−117.0	−21.0	−109.0	−19.8	−108.9	−19.6
	I	−109.6	−20.5	−104.3	−19.2	−105.0	−19.0
In	F	−129.7	−19.0	−120.6	−18.0	−119.5	−17.0
	Cl	−121.9	−19.4	−113.0	−18.9	−112.8	−18.3
	Br	−128.8	−19.3	−121.9	−18.6	−121.9	−18.1
	I	−125.8	−18.8	−120.3	−17.8	−121.0	−17.5

Table 7. Comparison of the Experimental and Theoretical Thermodynamic Characteristics for the Model Gas Phase Reactions $MH + HX = H_2 + MX$ (Standard Enthalpies in kJ mol^{-1}, Standard Entropies in J mol^{-1} K^{-1})[a]

		$\Delta H°_{298}$			$\Delta S°_{298}$		
M	X	theory	expt[c]	$\Delta\Delta H°_{298}$[b]	theory	expt[c]	$\Delta\Delta S°_{298}$[b]
Al	F	−255.9	−250.7 ± 7.9	−5.2	−16.1	−15.6 ± 0.05	−0.5
	Cl	−207.2	−211.7 ± 10.7	4.4	−16.1	−15.9 ± 0.06	−0.2
	Br	−205.6	−211.2 ± 22.3	5.6	−16.1	−16.1 ± 0.11	0.1
	I	−191.7	−220.4 ± 22.3	28.7	−15.6	−15.6 ± 0.40	0.0
Ga	F	−211.1	−173.5 ± 17.9	−37.6	−15.8	−15.0 ± 0.03	−0.8
	Cl	−192.6	−204.8 ± 14.3	12.2	−15.5	−15.8 ± 0.05	0.3
	Br	−197.2	−215.4 ± 14.3	18.2	−15.6	−16.0 ± 0.06	0.4
	I	−191.0	−224.7 ± 21.9	33.7	−15.3	−15.9 ± 0.06	0.6
In	F	−199.0	−136.2 ± 17.8	−62.8	−15.7	−14.4 ± 0.05	−1.3
	Cl	−194.3	−192.5 ± 10.3	−1.8	−15.5	−15.4 ± 0.05	−0.1
	Br	−205.8	−215.7 ± 14.2	9.9	−15.7	−15.9 ± 0.09	0.2
	I	−203.9	−230.4 ± 14.2	26.5	−15.5	*d*	*d*

[a] All results were obtained at the B3LYP/LANL2DZ(d,p) level of theory. [b] Theoretical value minus experimental value. [c] Experimental values are evaluated from the standard formation enthalpies and standard entropies taken from ref 46. [d] Experimental value is not available.

cluster (reaction) and second its reaction with excess HX:

$$ {}^1/_n[XMYH]_n + HX = {}^1/_2[X_2MYH_2]_2 \qquad (7) $$

Thermodynamic parameters for reaction 7 in the case of $n = 6$ are given in Table 4. The dimeric species $[X_2MYH_2]_2$ are considered as a major product, because the existence of trimers $[X_2MYH_2]_3$ in the gas phase is disfavored by the entropy. Indeed, it has been shown experimentally that trimeric $[Me_2GaP\text{-}i\text{-}Pr_2]_3$ and $[Me_2InP\text{-}i\text{-}Pr_2]_3$ are converted into corresponding dimers upon vacuum sublimation.[47] As may be seen from Table 4, for halides reaction 7 is highly exothermic and leads to large negative Gibbs energies in conjunction with their formation. Despite the fact that the process of degradation is disfavored by the entropy, the actual temperatures at which the equilibrium constant equals 1 are too high (≥1100 K). Degradation reactions for the lower oligomers are even more exothermic compared to hexamers. It is concluded that in excess HX the substitution process may lead to formation of saturated dimeric or (at low temperatures) trimeric rings $[X_2MYH_2]_{2,3}$ for all hydrogen halides HX.

Note, however, that, in contrast to halide species, the reaction with hydrogen ($HX = H_2$) is *endothermic*. Examination of the Ga−N oligomers showed that for the case $X = CH_3$ the reaction

$$ {}^1/_n[CH_3GaNH]_n + CH_4 = {}^1/_2[(CH_3)_2GaNH_2]_2 $$

is also endothermic and disfavored by entropy.[21] Consequently, consideration of X = H may well reproduce qualitative trends in the behavior of organometallic species. $[HMYH]_n$ and $[(CH_3)MYH]_n$ oligomers are predicted to be unreactive toward the H_2 or CH_4. Therefore, an excess of H_2 or CH_4 does not affect the oligomer formation, while an

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(47) Cowley, A. H. *J. Organomet. Chem.* **1990**, *400*, 71.

excess of HX precludes the equilibrium formation of hexamers due to cage degradation processes.

Finally, the stability of hexamer compounds with respect to the full cage degradation with formation of gaseous group 13 metal monohalides, hydrogen, and elemental pnictogen has been considered:

$$^{1}/_{6}[XMYH]_6 = MX + ^{1}/_{m}Y_m + ^{1}/_{2}H_2 \qquad (8)$$

($m = 2$ in the case of nitrogen; for phosphorus and arsenic $m = 4$). Results are summarized in Table 4. Process 8 is endothermic, but is very favorable in terms of entropy. Hydrogen-containing clusters have the highest stability toward cage degradation. For them, temperatures for which the equilibrium constant for process 8 equals 1 are given in Table 5. The stability of clusters decreases in the order Al > Ga > In; N > P > As. Under typical MOCVD conditions (900−1100 K) hexamer clusters in Al−N, Al−P, Al−As, Ga−N, and Ga−P systems should have considerable concentrations in the gas phase if thermodynamic equilibria were achieved. Their presence in the gas phase should not be neglected, especially when a detailed modeling of the CVD process is undertaken. We conclude that hydrogen-containing or organometallic hexamer clusters can be spontaneously formed in the gas phase under CVD conditions, which makes them natural SSP for the production of 13−15 materials.

Conclusions

Structural and thermodynamic parameters for the inorganic heterocyclic compounds $[XMYH]_n$ (M = Al, Ga, In; Y = N, P, As; X = H, F, Cl, Br, I; $n = 1-6$) have been predicted at the B3LYP/LANL2DZ(d,p) level of theory. Comparison of the structural parameters reveals common trends in the M−Y bond distances for all species considered. Thermodynamic analysis of the gas-phase reactions shows that formation of oligomers $[XMYH]_n$ in the gas phase is thermodynamically favorable for X = H but unfavorable in the case of X = F−I. Therefore, direct synthesis of the halide-containing imido compounds from MX_3 and NH_3 is not favorable. Substitution of the hydrogen atom in $[HMYH]_6$ by reaction with HX is thermodynamically favorable, but is countered by the very favorable cage degradation reactions with formation of the $[X_2MYH_2]_2$ amido dimers. In contrast to HX, processes of cage degradation are endothermic for H_2 and CH_4. Thus, imido compounds are stable toward the cage destruction in hydrogen or methane atmospheres. The high stability of the hydrogen-containing hexamers makes synthesis of the mixed-metal/mixed-pnictogen hexamers very promising with respect to future use as SSP for the production of 13−15 composites.

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Supporting Information Available: Tables giving the most important structural parameters of $[XMYH]_n$ species, theoretical harmonic vibrational frequencies and IR intencities for all studied compounds (B3LYP/LANL2DZ(d,p) level of theory, unscaled), and a figure presenting correlation between the Al−Y and Ga−Y/In−Y bond distances. This material is available free of charge via the Internet at http://pubs.acs.org.

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