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Ab Initio Molecular Orbital Investigation of the Amine-Alanes $(CH_3)_nH_{3-n}AlNX_3$ and Phosphane-Alanes $(CH_3)_nH_{3-n}AlPX_3$ ($X = H$, F, and Cl; $n = 0-3$) Complexes

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We report on ab initio calculations at the G2(MP2) level of the structures and Al−N(P) bond complexation energies of the $(CH_3)_nH_{3-n}AlNX_3$ and $(CH_3)_nH_{3-n}AlPX_3$ ($X = H$, F, and Cl; $n = 0-3$) donor−acceptor complexes. For the $(CH_3)_3AlNX_3$ and $(CH_3)_3AlPX_3$ complexes, the C_{3v} symmetry is found to be favored, and for the other complexes the C_s symmetry is found to be favored. The G2(MP2) calculated complexation energies show for the amine ligands the trend $NH_3 > NCl_3 > NF_3$. A similar trend $PH_3 \approx PCl_3 > PF_3$ is predicted for the phosphane ligands. The NBO partitioning scheme shows that there is no correlation between the stability and the charge transfer.

Introduction

It is known that the binding interaction between an electron pair donor (Lewis base) and an electron pair acceptor (Lewis acid) plays an important role in many chemical processes. The reaction takes place with formation of donor−acceptor complexes. It is also well known that Lewis acids have been known to act as catalysts in organic reactions. Indeed, there is substantial current interest in adducts based on main group acceptor atoms, such as B, Al, or Ga, and group 15 donor atoms, such as N, P, or As. Theses complexes are volatile, readily prepared in high purity, and can be decomposed either thermally or by laser irradiation.[1−15] On the other hand, the types of reactions in which trivalent aluminum plays a catalytic role are many and varied. However, complexes formed by aluminum trihalides (AlX_3) with various donor systems including organic molecules have attracted a lot of attention.[16−29] The points that have been more developed are conformational structure, complexation energy, charge decomposition analysis and degree charge transfer, and the role of the terminal atoms in several donor−acceptor complexes. A recent review about the analysis of the chemical bond in donor−acceptor complexes, including AlX_3, has been reported.[30] Recently, we reported[31] an ab initio molecular orbital study of X_3AlYH_3 ($X = F$, Cl, and Br; $Y =$ N, P, and As) complexes. We showed that the stability of these complexes does not depend on the charge transfer, whereas a correlation between the complexation energy and the corresponding donor fragment proton affinity has been observed. We have also shown that the NH_3 complexes with AlX_3 Lewis acids are more strongly bound than the respective PH_3 and AsH_3 complexes. In continuation of our work, we report now our investigation on the $(CH_3)_nH_{3-n}AlNX_3$ and $(CH_3)_nH_{3-n}AlPX_3$ ($X = H$, F, and Cl; $n = 0-3$) donor−acceptor complexes. Despite many theoretical works, no comparative ab initio studies of these complexes have been carried out. Our interest in these complex types originates from a development of a new class of main-group element ring and cage compounds as well as to define a new approach toward Al/N/AlP materials. The geometry and electronic structure of these complexes have been analyzed, and the relative stability and the substituent effect are examined.

Computational Details

Ab initio calculations were performed using the Gaussian 03 program.[32] Geometry optimizations were performed at the MP2(full)/6-31G(d) level; the zero-point vibrational energies (ZPE) were obtained from scaled HF/6-31G(d) frequencies (scaled by the factor 0.893).[33] For improved energy, the G2(MP2) energies[34] were computed. The electronic structure has been determined using the natural bond orbital (NBO)[35] partitioning analysis at the MP2(full)/6-31G(d) level. An important feature of the NBO method is that, unlike other charge partitioning schemes, the presence of diffuse functions in the basis sets does not affect the result.[35]

Results and Discussion

Association of $(CH_3)_nH_{3-n}Al$ ($n = 0-3$; C_{3h} symmetry), which act as electron pair acceptors, with $N(P)Y_3$ (C_{3v} symmetry; $X = H$, F, and Cl), which act as electron pair donors, leads to $(CH_3)_nH_{3-n}AlN(P)X_3$ (C_{3v} symmetry for $H_3AlN(P)X_3$ and $(CH_3)_3AlN(P)X_3$ complexes and C_s symmetry for the others complexes). Tables 1 and 2 list relevant optimized bond lengths and bond angles for all of the complexes studied in this work. The depicted geometrical parameters are reported in Figure 1. Tables 3 and 4 list, respectively, the computed complexation energies for the $(CH_3)_nH_{3-n}AlNX_3$ and $(CH_3)_nH_{3-n}AlPX_3$ ($X = H$, F, and Cl; $n = 0-3$) donor−acceptor complexes and the charge transfer from Lewis bases to Lewis acids (Q_t). The complexation energies are calculated as the difference between the energies of the complexes and the respective donor−acceptor moieties.

One can see from Table 1 that the Al−N equilibrium bond lengths in the NF_3 complexes are much longer than those found in NH_3 and NCl_3. In the PH_3 and PCl_3 complexes (Table 2), the optimization leads to an Al−P equilibrium bond length mush longer than that found in the PF_3 complexes. Upon methyl substitution, we can see a lengthening of the Al−N and Al−P

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TABLE 1: Selected Optimized Geometries (Bond Lengths in angstroms and Bond Angles in deg) of $(CH_3)_nH_{3-n}AlNX_3$ (X = H, F, and Cl; $n = 0-3$)

compound	Al−N	Al−C	Al−H	N−X	∠H−Al−N	∠C−Al−N	∠Al−N−X	∠X−N−X
H_3AlNH_3	2.083		1.606	1.020	99.43		111.35	107.52
$CH_3H_2AlNH_3$	2.088	1.982	1.614	1.020	98.67	101.02	111.06	107.49
				1.020				107.56
$(CH_3)_2HAlNH_3$	2.092	1.985	1.616	1.020	98.02	100.28	111.17	107.51
							111.80	107.45
$(CH_3)_3AlNH_3$	2.098	1.989		1.020		99.67	111.43	107.45
H_3AlNF_3	2.304		1.592	1.369	93.56		115.33	103.01
$CH_3H_2AlNF_3$	2.318	1.966	1.597	1.371	93.07	94.67	114.72	102.94
				1.369			116.53	103.07
$(CH_3)_2HAlNF_3$	2.331	1.969	1.601	1.370	92.50	94.40	115.92	103.02
				1.372			114.33	102.90
$(CH_3)_3AlNF_3$	2.344	1.973		1.372		94.10	115.46	
H_3AlNCl_3	2.215		1.596	1.762	95.89		110.49	104.43
$CH_3H_2AlNCl_3$	2.233	1.970	1.600	1.764	94.65	99.10	110.82	108.27
				1.763			110.23	108.29
$(CH_3)_2HAlNCl_3$	2.250	1.973	1.605	1.764	93.55	98.06	110.60	108.12
				1.765			111.05	108.14
$(CH_3)_3AlNCl_3$	2.272	1.977		1.765		97.08	110.92	107.98

TABLE 2: Selected Optimized Geometries (Bond Lengths in angstroms and Bond Angles in deg) of $(CH_3)_nH_{3-n}AlPX_3$ (X = H, F, and Cl; $n = 0-3$)

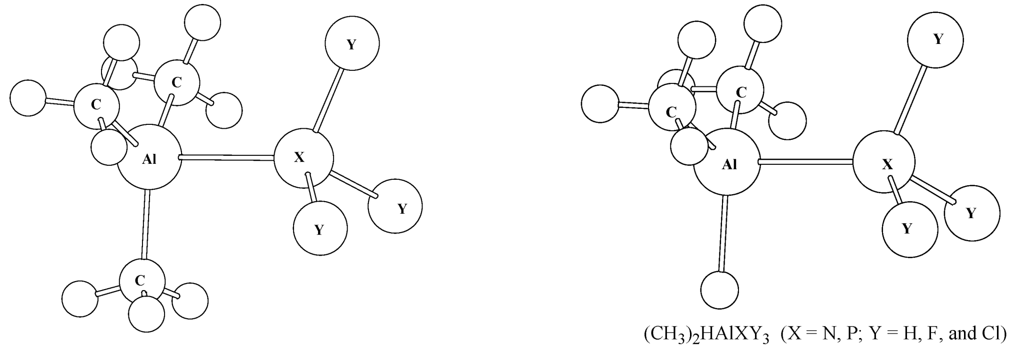
compound	Al−P	Al−C	Al−H	P−X	∠H−Al−P	∠C−Al−P	∠Al−P−X	∠X−P−X
H_3AlPH_3	2.545		1.601	1.405	97.28		118.49	99.14
$CH_3H_2AlPH_3$	2.563	1.979	1.606	1.407	96.05	100.36	118.20	98.88
				1.406			118.96	98.77
$(CH_3)_2HAlPH_3$	2.584	1.981	1.611	1.407	95.00	99.12	118.64	98.64
				1.407			119.48	98.53
$(CH_3)_3AlPH_3$	2.606	1.984		1.408		98.07	119.12	98.31
H_3AlPF_3	2.530		1.595	1.574	94.32		117.88	99.89
$CH_3H_2AlPF_3$	2.546	1.974	1.600	1.576	93.18	97.51	118.21	99.77
							117.92	99.62
$(CH_3)_2HAlPF_3$	2.563	1.976	1.605	1.577	91.97	96.53	118.05	99.67
				1.578			118.29	99.53
$(CH_3)_3AlPF_3$	2.582	1.979		1.579		95.48	118.23	99.46
H_3AlPCl_3	2.558		1.597	2.025	94.23		115.28	103.09
$CH_3H_2AlPCl_3$	2.574	1.973	1.602	2.029	92.99	97.09	116.04	102.99
				2.026			115.10	102.78
$(CH_3)_2HAlPCl_3$	2.594	1.976	1.607	2.029	91.92	95.98	115.89	102.87
				2.032			114.85	102.70
$(CH_3)_3AlPCl_3$	2.617	1.979		2.033		97.98	115.67	102.61

bonds. The trends of the Al−C, Al−H, N−X, and P−X bonds are similar in all complexes.

On the other hand, the bond angles −H−Al−N(P) and −H−Al−N(P) vary slightly in going from AlX_3 free moiety (90°) to $X_3AlY(CH_3)_3$ complex adduct. It increases only by about ∼2−11°. This has a consequence for the Al geometrical environment, which passes from D_{3h} (flat) in free AlX_3 to pseudo-pyramidal in the complex. For the bond angles −X−N(P)−X and −C−Al−C, we note no notable deviation in going from isolated $(CH_3)_nH_{3-n}Al$ to $(CH_3)_nH_{3-n}AlNX_3$ and $(CH_3)_nH_{3-n}AlPX_3$ complexes. One can see that the −X−Al−X bond angle decreases by about 4° in going from the isolated $(CH_3)_nH_{3-n}Al$ ($n = 0-3$) ligands to the complex adducts. The −X−N(P)−X bond angle increases by about 1° in going from the isolated $N(P)X_3$ ligand to the complex adduct.

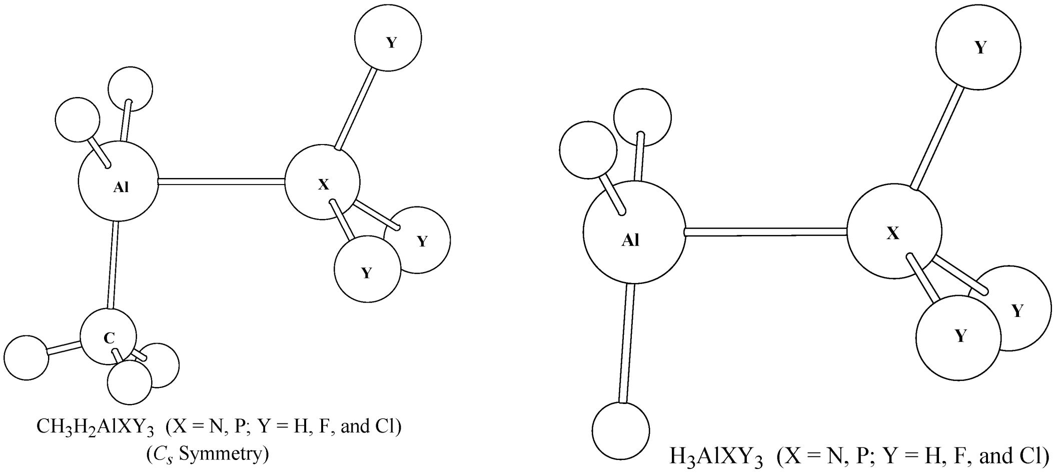
The G2(MP2) calculations predict that the Lewis acids $(CH_3)_nH_{3-n}Al$ form a strongly bonded complex with the Lewis base NH_3 but not with NF_3 and BCl_3. Indeed, Figure 2 shows nicely that NH_3 leads always to the more stable complex among the Lewis bases. This is in agreement with calculated HOMO−LUMO gaps that increase on going from NH_3 or NCl_3 to NF_3 (the energies of the HOMO are −0.431, −0.429, and −0.567 au for NH_3, NCl_3, and NF_3, respectively, obtained at the 6-311+G(3df,2p) level of theory). Indeed, the G2(MP2) calculated complexation energies show for the amine ligands the trend $NH_3 > NCl_3 > NF_3$. On the other hand, it has been found for the NH_3 complexes that the introduction of the first methyl group on aluminum atom destabilizes the complex by ∼1 kcal/mol, the second by ∼2 kcal/mol, and the third by ∼3 kcal/mol. Hence, the calculations predict that successive methyl substitution on aluminum reduces slightly the complexation energies. Indeed, the methyl substitution reduces slightly the Lewis acid strength of the alanes. For the NF_3 and NCl_3 complexes, the successive methyl substitution on aluminum atom has little effect on the stability of the complexes. This trend is justified by a more steric bulk in these complexes. Nevertheless, substitution of hydrogen by methyl in all of the compounds shows a striking difference between Lewis bases. The same trends have been observed for the transferred charge. Indeed, the charge transfer from NH_3 to AlX_3 (X = F, Cl, and Br) is lower than that from NF_3 and NCl_3. On the other hand, the methyl substitution does not affect the relative transferred charge (Table 3), and there is no correlation between the stability and the transferred charge.

In the phosphane complexes, the calculations predict that the Lewis acids $(CH_3)_nH_{3-n}Al$ form strong bonded complexes with the Lewis base PH_3 and PCl_3 but not with PF_3. This is in agreement with calculated HOMO−LUMO gaps that increase on going from PH_3 or PCl_3 to NF_3 (the energies of the HOMO



$(CH_3)_3AlXY_3$ (X = N, P; Y = H, F, and Cl)
(C_{3V} Symmetry)

$(CH_3)_2HAlXY_3$ (X = N, P; Y = H, F, and Cl)
(C_s Symmetry)



$CH_3H_2AlXY_3$ (X = N, P; Y = H, F, and Cl)
(C_s Symmetry)

H_3AlXY_3 (X = N, P; Y = H, F, and Cl)
(C_{3V} Symmetry)

Figure 1. Optimized structures of the $(CH_3)_nH_{3-n}AlN(P)X_3$ (X = H, F, and Cl; n = 0−3) complexes.

TABLE 3: G2(MP2) Complexation Energies (E_{comp} in kcal/mol) of $(CH_3)_nH_{3-n}Al$ Acceptor with NY_3 (X = H, F, and Cl) Donor and Charge Transfer Q_t (Electron) from Donor to Acceptor

complex	$E_{comp}^{a,b}$	Q_t
H_3AlNH_3	−25.23	0.170
$CH_3H_2AlNH_3$	−24.17	0.171
$(CH_3)_2HAlNH_3$	−23.26	0.173
$(CH_3)_3AlNH_3$	−22.41	0.175
H_3AlNF_3	−5.06	0.107
$CH_3H_2AlNF_3$	−5.24	0.105
$(CH_3)_2HAlNF_3$	−5.47	0.104
$(CH_3)_3AlNF_3$	−5.71	0.104
H_3AlNCl_3	−12.90	0.109
$CH_3H_2AlNCl_3$	−13.33	0.108
$(CH_3)_2HAlNCl_3$	−13.74	0.109
$(CH_3)_3AlNCl_3$	−14.07	0.111

[a] $E_{comp} = E((CH_3)_nH_{3-n}AlPX_3) - [E((CH_3)_nH_{3-n}Al) + E(PX_3)]$ (X = H, F, and Cl). [b] Including ZPE corrections.

TABLE 4: G2(MP2) Complexation Energies (E_{comp} in kcal/mol) of $(CH_3)_nH_{3-n}Al$ Acceptor with PY_3 (X = H, F, and Cl) Donor and Charge Transfer Q_t (Electron) from Donor to Acceptor

complex	$E_{comp}^{a,b}$	Q_t
H_3AlPH_3	−12.59	0.267
$CH_3H_2AlPH_3$	−11.48	0.262
$(CH_3)_2HAlPH_3$	−10.57	0.258
$(CH_3)_3AlPH_3$	−9.87	0.253
H_3AlPF_3	−6.58	0.317
$CH_3H_2AlPF_3$	−6.00	0.310
$(CH_3)_2HAlPF_3$	−5.59	0.304
$(CH_3)_3AlPF_3$	−5.34	0.297
H_3AlPCl_3	−13.80	0.214
$CH_3H_2AlPCl_3$	−13.90	0.207
$(CH_3)_2HAlPCl_3$	−14.15	0.201
$(CH_3)_3AlPCl_3$	−14.59	0.196

[a] $E_{comp} = E((CH_3)_nH_{3-n}AlPX_3) - [E((CH_3)_nH_{3-n}Al) + E(PX_3)]$ (X = H, F, and Cl). [b] Including ZPE corrections.

are −0.385, −0.401, and −0.473 au for PH_3, PCl_3, and PF_3, respectively, obtained at the 6-311+G(3df,2p) level of theory). Indeed, the G2(MP2) calculations predict the trend $PH_3 \approx PCl_3 > PF_3$. On the other hand, it has been found that the methyl substitution on aluminum atom reduces slightly the stability of the PH_3 complexes. For the PF_3 and PCl_3 complexes, the successive methyl substitution on aluminum atom has little effect on the stability of the complexes. These effects are shown nicely in Figure 3. The same trends have been observed for the transferred charge. The NBO results listed in Table 4 show that the $(CH_3)_nH_{3-n}AlPF_3$ complexes have a higher charge transfer from PF_3 to $(CH_3)_nH_{3-n}Al$ acceptor moieties. They also show that methyl substitution does not affect the relative transferred charge (Table 4). Indeed, the charge transfer from NH_3 to AlX_3 (X = F, Cl, and Br) is lower than that from NF_3 and NCl_3.

On the other hand, we can see from results reported in Tables 3 and 4 that the complexes including N are more stable than those including P for $N(P)H_3$. This trend is justified by the fact that PH_3 is a weaker Lewis base than NH_3. However, for $N(P)X_3$ (X = F, Cl), the stabilities of the corresponding complexes with alanes are almost the same. It can be explained by the fact that the order of the Lewis acid strength of the alanes depends on the N(P) Lewis bases. Indeed, the HOMO−LUMO gaps become almost the same. Hence, the Lewis acid and Lewis base strengths are close.

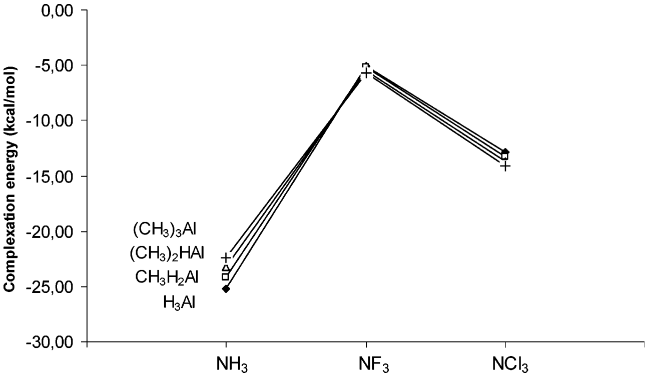


Figure 2. Trend of the calculated complexation energies of the $(CH_3)_nH_{3-n}AlNX_3$ (X = H, F, and Cl; $n = 0-3$) complexes.

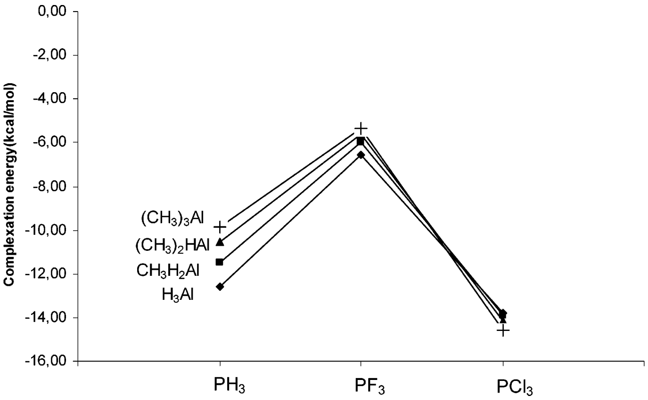


Figure 3. Trend of the calculated complexation energies of the $(CH_3)_nH_{3-n}AlPX_3$ (X = H, F, and Cl; $n = 0-3$) complexes.

Conclusion

Ab initio calculations have been carried out to study the interaction in $(CH_3)_nH_{3-n}AlNX_3$ and $(CH_3)_nH_{3-n}AlPX_3$ (X = H, F, and Cl; $n = 0-3$) donor−acceptor complexes. The calculation shows the trend $NH_3 > NCl_3 > NF_3$ at the G2(MP2) level of theory. With phosphane complexes, the predicted trend is $PH_3 \approx PCl_3 > PF_3$. The energetic results show that the substitution of hydrogen by methyl increases the stability of the $(CH_3)_nH_{3-n}AlNH_3$ and $(CH_3)_nH_{3-n}AlPH_3$ complexes and decreases $(CH_3)_nH_{3-n}AlNX_3$ and $(CH_3)_nH_{3-n}AlPX_3$ (X = F, Cl) complexes. The complexation processes have little effect on the structural parameters. The analysis of the electronic structure based on natural bond orbitals (NBO) indicates that there is no correlation between the charge transfer and the stability of the complex.

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