G2(MP2) Investigation of Alane-$[X(CH_3)_3]^-$ (X = C, Si, and Ge) and Alane-$Y(CH_3)_3$ (Y = N, P, and As) Interactions

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Alane-$[X(CH_3)_3]^-$ (X = C, Si, and Ge) and alane-$Y(CH_3)_3$ (Y = N, P, and As) have been investigated as donor−acceptor complex types at the G2(MP2) level of theory. The results show that the anionic complexes are more stable than the neutral ones. They show also that this stability decreases when going from carbon to germanium for $[H_3AlX(CH_3)_3]^-$ complexes and from nitrogen to arsenic for $H_3AlY(CH_3)_3$ complexes. The interaction diagrams prove that the evolution of complexation energy depends on the coordination mode. In fact, it is a result of two interaction types: interaction between "a_1" symmetry fragment molecular orbital (stabilizing) and interactions between "e" symmetry fragment molecular orbital (destabilizing). The NBO analysis suggests that there is no correlation between the charge transfer and the complexation energy. It also shows that the shortening of the X(Y)−C bond lengths, upon complexation, is due to the increasing "s" character of these bonds.

1. Introduction

Lewis acids have long been known as catalysts in organic reactions. The types of reactions in which trivalent aluminum plays a catalytic role are many and varied.[1−10] There have been a number of experimental and theoretical studies of donor−acceptor complexes involving AlH_3 and AlX_3 lewis acids.[11−28] Most of these studies involve chemistry and reactivity of alane adducts.

Our group has recently published interesting theoretical work on the anionic and neutral alane donor−acceptor complexes.[29,30] We have shown that the stability decreases when descending in the periodic table column. The interaction diagrams prove that the evolution of complexation energy depends on the coordination mode. On the other hand, we have shown that in the neutral borane and alane complexes, the donor−acceptor interaction was not based on a simple mixture HOMO−LUMO, but it's developed between three or four orbitals of the fragments.[29−31] We have also shown that there is no correlation between the complexation energy and the charge transfer. In continuation of our work we report now our investigation on the anionic alane donor−acceptor complexes $[H_3AlX(CH_3)_3]^-$ (X = C, Si, and Ge) compared to the isoelectronic neutral $H_3AlY(CH_3)_3$ (Y = N, P, and As) ones. The relative stabilities of these complexes are examined with respect to the qualitative molecular orbital analysis (QMOA).[32,33] The QMOA arguments have proven useful and successful for predicting the broad outlines of calculations.[29−33] The choice of the complexes investigated was made with the aim to include different types of strongly bound molecules (anionic one) and coordination compounds (neutral one). To the best of our knowledge, no comparative study of these complexes has been carried out. A computer search of *Chemical Abstract* (American Chemical Society: Washington, DC) did not offer any help in this matter.

2. Computational Details

Ab initio calculations were performed using the GAUSSIAN98 series of computer programs[34] on the IBM RS/6000 workstations of the University of València.

Geometry optimizations were performed at the MP2(full)/6-31G(d) level, the zero-point vibrational energies (ZPE) are obtained from scaled HF/6-31G(d) frequencies (scaled by the factor 0.893).[35] For improved energy, the G2(MP2) energies[36] were computed. The electronic structures have been done using the natural bond orbital (NBO)[37] partitioning scheme at the MP2(full)/6-31G(d) level. NBO's are the localized set of easily recognizable Lewis-like (σ and π bond, lone pair, and core) and non-Lewis (σ* and π* antibond and Rhydberg) orbitals, which are optimal in the sense of orthonormality and maximum occupancy of the Lewis set. 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.[37] On another hand, we did not correct for the basis set superposition errors (BSSE), which should be relatively small with a large basis set such as 6-311+G(3df,2p). Moreover, a study by Mikhali et al.,[38] using the G2(+) method, shows that the BSSE has a little effect on the calculated complexation energies.

3. Results and Discussion

Table 1 lists the most important optimized geometrical parameters of $[X(CH_3)_3]^-$ and $Y(CH_3)_3$ moieties and theirs corresponding complexes with alane at the MP2(full)/6-31G(d) level. All moieties and complexes have C_{3v} symmetry, and alane has D_{3h} symmetry.[27,28] Upon complexation, the MP2 Al−H bond length value is slightly longer than for isolated fragment. The bond angle ∠H−Al−(C_3 axis) pass from 90° in free acceptor AlH_3 to the tetrahedral value (∼108°) in the anionic compounds. In fact, the optimized values at the MP2(full)/6-31G(d) level are 108.8, 108.4, and 108.3° for [H$_3$AlC-

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TABLE 1: Selected Geometrical Parameters[a] of Free [X(CH$_3$)$_3$]$^-$ and Y(CH$_3$)$_3$ Ligands and Coresponding Complexes with AlH$_3$

compound	method[b]	Al−X(Y)	Al−H	X(Y)−C	∠H−Al−X(Y) or ∠H−Al−C_3 axis	∠H−Al−H	∠C−X(Y)−Al or ∠C−X(Y)−C_3 axis	∠C−X(Y)−C
[C(CH$_3$)$_3$]$^-$	MP2			1.505			111.3	107.6
[Si(CH$_3$)$_3$]$^-$	MP2			1.962			120.7	96.2
[Ge(CH$_3$)$_3$]$^-$	MP2			2.025			121.6	95.0
[H$_3$AlC(CH$_3$)$_3$]$^-$	MP2	2.052	1.650	1.527	108.8	110.2	110.5	108.4
[H$_3$AlSi(CH$_3$)$_3$]$^-$	MP2	2.503	1.643	1.919	108.4	110.5	115.0	103.4
[H$_3$AlGe(CH$_3$)$_3$]$^-$	MP2	2.518	1.640	1.976	108.3	110.7	116.3	101.8
N(CH$_3$)$_3$	MP2			1.453			108.5	110.4
P(CH$_3$)$_3$	MP2			1.849			118.5	99.1
As(CH$_3$)$_3$	MP2			1.953			120.4	96.7
H$_3$AlN(CH$_3$)$_3$	MP2	2.074	1.609	1.478	100.0	117.1	109.3	109.6
	CISD[c]	2.063	1.585	1.474	99.9	117.1	109.4	109.5
	exptl[d]	2.063	1.560	1.476	104.3	114.1	109.0	109.2
H$_3$AlP(CH$_3$)$_3$	MP2	2.463	1.610	1.828	99.5	117.4	114.7	103.8
H$_3$AlAs(CH$_3$)$_3$	MP2	2.538	1.608	1.933	99.6	117.3	117.0	101.0

[a] All distances in angstroms, angles in degrees. [b] MP2(full)/6-31G(d) calculations. The computed Al−H parameter of free ALH$_3$ is 1.589 Å. [c] CISD/DZP calculations from ref 27. [d] Electron diffraction values from ref 24.

(CH$_3$)$_3$]$^-$, [H$_3$AlSi(CH$_3$)$_3$]$^-$, and [H$_3$AlGe(CH$_3$)$_3$]$^-$, respectively. For the H$_3$AlY(CH$_3$)$_3$ complexes the bond angle ∠H−Al−(C$_3$ axis) varies slightly in going from free ligand to adduct. The optimized values at the same level are 100.0, 99.5, and 99.6° for H$_3$AlN(CH$_3$)$_3$, H$_3$AlP(CH$_3$)$_3$, and H$_3$AlAs(CH$_3$)$_3$, respectively. We can by now conclude that the donor behavior is not the same in the two series. Moreover, the Al−X (X = C, Si, and Ge) bond have a covalent character. This has a consequence on the Al geometrical environment, which pass from D_{3h} (flat) in free AlH$_3$ to Td (pyramidal) in the complex. Nevertheless, the equivalent Al−Y (Y = N, P, and As) bond has not such strong effect on the AlH$_3$ fragment's geometry in the complex. The ∠H−Al−(C$_3$ axis) bond angle increases only by about 9° in going from isolated AlH$_3$ to H$_3$AlY(CH$_3$)$_3$ complex, while this variation is about 18° in the anionic adducts. If we take into account both behaviors, the Al−Y bond length trend and the negligible geometry variation of the AlH$_3$ fragment, we can conclude also that the Al−Y (Y = N, P, and As) bond has no covalent character. This result allows us to indicate the existence of a weak interactions in the neutral donor−acceptor complexes and strong interactions in the anionic ones. The same trend has been observed in the [H$_3$AlXH$_3$]$^-$ (X = C, Si, and Ge) and H$_3$AlYH$_3$ (Y = N, P, and As) hydrogenated complexes.[29]

Concerning the bond angles ∠C−X−Al and ∠C−Y−Al, there is no notable deviation between the two compound sets. For the anionic ones, the MP2(full)/6-31G(d) optimized values are 110.5°, 115.0°, and 116.3° (Table 1) for [H$_3$AlC(CH$_3$)$_3$]$^-$, [H$_3$AlSi(CH$_3$)$_3$]$^-$, and [H$_3$AlGe(CH$_3$)$_3$]$^-$, respectively, while in the free ligand [X(CH$_3$)$_3$]$^-$, this angle is 111.3, 120.7, and 121.6° for [C(CH$_3$)$_3$]$^-$, [Si(CH$_3$)$_3$]$^-$, and [Ge(CH$_3$)$_3$]$^-$, respectively. One can see that the largest deviation is about 5° in going from the isolated ligand to the complex adduct. For the Y(CH$_3$)$_3$(Y = N, P, and As) case, the MP2(full)/6-31G(d) bond angle values in the complex adducts are 109.3, 114.7, and 117.0°, respectively, and in isolated ligands N(CH$_3$)$_3$, P(CH$_3$)$_3$, and As(CH$_3$)$_3$ are 108.5, 118.5, and 120.4°, respectively. In this case, the deviation is about 4°. Therefore, there is the same complexation effect on the [X(CH$_3$)$_3$]$^-$ (X = C, Si, and Ge) ligands as well as Y(CH$_3$)$_3$ (Y = N, P, and As) ones. On the other hand our calculated geometrical parameters for the TMAA molecule are in good agreement with experimental values, and with previous accurate calculations (see Table 1).

Of particular interest is the X(Y)-C bond distance. On complex formation, the calculated geometrical parameters show a lengthening of the C−C and N−C bonds, that seems consistent with a chemical intuition. A striking feature is the shortening of the X−C (X = Si and Ge) and Y−C (Y = P and As) bonds. To explain this result, we have applied the NBO analysis at MP2(full)/6-31G(d) level of theory. However, the NBO calculations show that in isolated donor fragments, the lone pair on X(Y) (X = Si and Ge and Y = P and As) atoms has lower "s" character than that in complexes. Taking into account that the "s" character favors the bond consistency, we can deduce that this change alone would imply a shortening of the X−C and the Y−C bond lengths because it increases upon coordination. Moreover, Table 2 shows that the 3s and 4s atomic orbital (AO) contribution of Si (or P) and Ge (or As), respectively, in the Si(or P)−C and Ge(or As)−C bonds is more important in [H$_3$AlX(CH$_3$)$_3$]$^-$ and H$_3$AlY(CH$_3$)$_3$ complexes than that in isolated [X(CH$_3$)$_3$]$^-$ (X = Si and Ge) and Y(CH$_3$)$_3$ (Y = P and As) moieties. These trends are substantiated by other theoretical or experimental results.[39−43]

TABLE 2: MP2(full)/6-31G(d) Calculated X(Y)−C Bond Lengths (Å) of [H$_3$AlX(CH$_3$)$_3$]$^-$ and H$_3$AlY(CH$_3$)$_3$ Complexes and Their Isolated Ligands and ns MP2(full)/6-31G(d)-NBO Contribution of X(Y) Atoms in the X(Y)−C Bonds (%)

	X(Y)−C	ns$_{(X(Y)-C)}$[a]
[C(CH$_3$)$_3$]$^-$	1.505	27.17
[H$_3$AlC(CH$_3$)$_3$]$^-$	1.527	25.65
[Si(CH$_3$)$_3$]$^-$	1.962	14.71
[H$_3$AlSi(CH$_3$)$_3$]$^-$	1.919	22.82
[Ge(CH$_3$)$_3$]$^-$	2.025	12.92
[H$_3$AlGe(CH$_3$)$_3$]$^-$	1.976	23.43
N(CH$_3$)$_3$	1.453	27.58
H$_3$AlN(CH$_3$)$_3$	1.478	26.86
P(CH$_3$)$_3$	1.849	16.20
H$_3$AlP(CH$_3$)$_3$	1.828	23.00
As(CH$_3$)$_3$	1.953	13.46
H$_3$AlAs(CH$_3$)$_3$	1.933	21.91

[a] n = 2, 3, and 4, respectively, for (C and N), (Si and P), and (Ge and As) atoms.

In Table 3, we give the G2(MP2) calculated complexation energies of the [H$_3$AlX(CH$_3$)$_3$]$^-$ (X = C, Si, and Ge) and H$_3$AlY(CH$_3$)$_3$ (Y = N, P, and As) complexes and the NBO-MP2(full)/6-31G(d) charge transfer. The complexation energies are calculated as the differences between the complexes and the respective donor−acceptor moieties. To evaluate the effect of methyl substitution, we also give in Table 3 the G2(MP2) calculated complexation energies and the NBO-MP2(full)/6-31G(d) charge transfer of the [H$_3$AlXH$_3$]$^-$ (X = C, Si, and Ge) and H$_3$AlYH$_3$ (Y = N, P, and As) complexes.[29] G2(MP2) results show that the anionic [H$_3$AlX(CH$_3$)$_3$]$^-$ (X = C, Si, and Ge) complexes are more stable than the neutral H$_3$AlY(CH$_3$)$_3$ (Y =

TABLE 3: G2(MP2) Complexation Energies (E_{comp} in kcal/mol) and Charge Transfer Qc(electron)

complex[a]	E_{comp}[b]	Qc
$[H_3AlC(CH_3)_3]^-$	−80.17(−84.68)	0.337(0.338)
$[H_3AlSi(CH_3)_3]^-$	−59.80(−54.42)	0.643(0.577)
$[H_3AlGe(CH_3)_3]^-$	−52.79(−49.88)	0.613(0.536)
$H_3AlN(CH_3)_3$	−32.08(−25.24)	0.147(0.132)
$H_3AlP(CH_3)_3$	−25.06(−12.60)	0.305(0.237)
$H_3AlAs(CH_3)_3$	−19.45(−9.75)	0.313(0.239)

[a] The reported values in parentheses correspond to the nonmethylated complexes. (From ref 29.) [b] $E_{\mathrm{comp}} = E(H_3AlL) - [E(H_3Al) + E(L)]$ with $L = [X(CH_3)_3]^-$, (X = C, Si, and Ge) and $L = Y(CH_3)_3$ (Y = N, P, and As).

N, P, and As) ones. However, the complexation energy decreases for each group in going from C (or N) to Ge (or As). The complexation energy decreases thus, when descending in the corresponding periodic table column. Therefore, the anionic donor−acceptor complexes show rather strong donor−acceptor bonds when one compares to the neutral adduct ones. These values can be explained since $[H_3AlC(CH_3)_3]^-$, $[H_3AlSi(CH_3)_3]^-$, and $[H_3AlGe(CH_3)_3]^-$ are isoelectronic to the corresponding stable organic compounds $H_3CC(CH_3)_3$, $H_3CSi(CH_3)_3$, and $H_3CGe(CH_3)_3$, respectively, and the HOMO orbital of the anionic ligands is close to the AlH_3 LUMO one (see below). Furthermore, in the anionic complexes, the donor central atom X is in its preferred coordination. From the NBO-MP2(full)/6-31G(d) analysis (Table 3), we note that there is no correlation between charge transfer and the G2(MP2) complexation energy for the two series of complexes as recently evoked in our previously works.[29,30] This conclusion is also in agreement with Schaefer et al.'s computational study on their investigations of the role of the terminal atoms in donor−acceptor complexes formation of group 13 metal halides.[44] For the most stable anionic complex $[H_3AlC(CH_3)_3]^-$ the charge transferred is 0.337e while for the less stable one $[H_3AlGe(CH_3)_3]^-$ this charge is 0.613e. We note also the same trend for the neutral complexes.

On the other hand, by methyl substitution on central atom (X or Y) of the donor fragment, the complexation energy and the charge transfer increase. This effect is more important for the neutral complexes. Indeed, the methyl substitution stabilizes the complex by ∼7, ∼13, and ∼10 kcal/mol for $H_3AlN(CH_3)_3$, $H_3AlP(CH_3)_3$, and $H_3AlAs(CH_3)_3$ complexes, respectively. The charge-transfer varies in the even feel as the complexation energies (Table 3).

We apply now QMOA to examine the factors behind the stabilization upon coordination and show which fragment orbitals are implicated in construction bond between aluminum and Y atoms (Y = central atom of the donor fragment). The characteristics of the chemical bond under consideration in the complexes will be discussed from ab initio calculations at the HF/STO-3G level of theory (this basis set has been chosen only for qualitative investigations). In all correlation diagrams, the molecular orbitals of alane AlH_3 and the donor ligands were taken in the symmetry of the corresponding complexes. In this section we will not discuss the coordination mode of the anionic compounds $[H_3AlX(CH_3)_3]^-$ (X = C, Si, and Ge) because it is based mainly on a classical HOMO−LUMO interaction mode which is well-known. For all neutral compounds the complexation is controlled by the presence of two interaction types. The first one takes place between the "a_1" symmetry orbitals likely to interact along the axis of Al−Y bond (i.e., a three-level and four-electron model system)[31] and the second one uses the "e" symmetry orbitals whose the character is rather destabilizing because they are all occupied(i.e., a two-level and four-electron model system).[31] As we have shown in our previous work,[29] in the "a_1" orbitals interaction, there are three fragment molecular orbitals for $H_3AlN(CH_3)_3$ complex and four fragment molecular orbitales for $H_3AlP(CH_3)_3$ and $H_3AlAs(CH_3)_3$ complexes that interact between themselves. This interaction is globally stabilizing. Nevertheless, the "e" interaction is destabilizing because it is developed between occupied fragment molecular orbitals. But why the complexation energy decreases on going from N to As atoms? The answer to this question is related, on one hand, to the HOMO(donor)-LUMO(acceptor) energetic gap and, on another hand, to the "e"(acceptor) and "e"(donor) energetic position. In fact, the energetic difference $E(\mathrm{LUMO}) - E(\mathrm{HOMO})$ decreases on going from N to As fragments what lets think that the stabilizing interaction increases in this feel, but the destabilizing "e" interaction increases since the corresponding gap $[E(\text{“e”(acceptor)}) - E(\text{“e”(donor)})]$ also decreases. The destabilizing character becomes thus more important on going from N to As and the complexation energy is also decreasing.

Let's now examine the methyl substitution effect on the coordination mode. Thanks to methyl groups, the $Y(CH_3)_3$ fragment molecular orbital that is mainly concerned by the coordination is closer to the AlH_3 LUMO than that in the YH_3 case. Hence, the interaction is more favored with a methylated ligand than that with a hydrogenated one. We can thus conclude that the complexes resulting from methylated ligands are more stable than those resulting from analogous hydrogenated ones. This is in agreement with the computed complexation energy and charge transfer. However, taking adducts by couple (H_3AlYH_3, H_3AlYMe_3), we notice that the complexation energy is higher for the methylated adducts than that of the hydrogenated ones. The same observation could be made for the charge transferred (Table 3). The donor character of the methyl group favors the coordination by transferring more charge from the donor to the acceptor.

4. Conclusion

G2(MP2) calculations have been carried out to analyze the nature of the interaction in various donor−acceptor complexes (alane-$[X(CH_3)_3]^-$ (X = C, Si, and Ge) and alane-$Y(CH_3)_3$ (Y = N, P, and As)). For the neutral adducts the stability decreases irregularly while descending in the corresponding column of the ligand central atom. It is a consequence of two interactions that take place between the two fragment molecular orbitals (donor and acceptor). The first one is stabilizing and developed between "a_1" symmetry molecular orbitals whereas the second one has a destabilizing character and it is developed between molecular orbitals having "e" symmetry. In the anionic complexes, the mode of coordination is controlled mainly by the well-known HOMO−LUMO interaction. The energetic results show that the methyl substitution increases the stability of the complexes investigated in this work. Upon complexation, the structural parameters of alane-$[X(CH_3)_3]^-$ (X = Si and Ge) and alane-$Y(CH_3)_3$ (Y = P and As) complexes show an irregular shortening of the X(Y)−C bonds. The analysis of the electronic structure based on natural bond orbitals (NBO) partitioning scheme shows that this shortening was related to the increasing of the 's' character in these bonds. It also indicates that there is no correlation between the charge transfer and the calculated complexation energies.

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