Unexpected Acidity Enhancement Triggered by AIH(3) Association to Phosphines

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Unexpected Acidity Enhancement Triggered by AlH₃ Association to Phosphines

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Ⓢ *Supporting Information*

ABSTRACT: The complexes formed by the interaction between a series of phosphines R—PH$_2$ (R = H, CH$_3$, c-C$_3$H$_5$, C$_6$H$_5$) and AlH$_3$ have been investigated through the use of high-level G4 ab initio calculations. These very stable complexes behave as much stronger acids than the isolated phosphines. This dramatic acidity enhancement, which can be as high as 174 kJ mol^{-1}, results from a much greater stabilization of the anionic deprotonated species with respect to the neutral one, upon AlH$_3$ association. This effect depends quantitatively on the nature of the substituent R and is smaller for R = C$_6$H$_5$ because of the conjugation of the P lone pair with the aromatic system. More unexpectedly, however, the phosphine—alane complexes, RPH$_2$:AlH$_3$, are more acidic than the corresponding phosphine—borane RPH$_2$:BH$_3$ analogues. This unexpected result is due to the enhanced stability of the anionic deprotonated species for complexes involving AlH$_3$, because the delocalization of the newly created P lone pair with the P—Al bonding density is more favorable when the Lewis acid is aluminum trihydride than when it is borane.
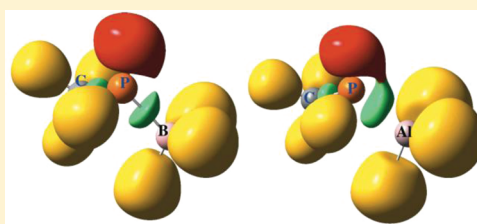
INTRODUCTION

Although noncovalent interactions play a significant role in nature,[1−4] and they are present in most of the known molecular assemblies, there is not a clear-cut definition of them.[5] Typically, most of these interactions, such as hydrogen bonds,[6−13] halogen bonds,[14−17] beryllium bonds,[18] metal ion—molecule complexes,[19−31] van der Waals complexes,[32−36] etc., involve closed-shell species. This would permit a first distinction between noncovalent interactions and typical covalent bonds which usually involve the interaction between open-shell systems. Nevertheless, in most of the aforementioned examples of noncovalent interactions, some charge transfer between the two interacting moieties takes place. These partial charge transfers go from the lone pair of one of the interacting subunits, which behave as a Lewis base (in a hydrogen-bond complex the proton acceptor), toward empty orbitals of the other interacting subunit, acting as a Lewis acid (in a hydrogen-bond complex, the proton donor). These charge donations can be very strong in those cases in which the electron acceptor has low-lying empty orbitals and therefore behaves as a strong Lewis acid. This is typically the case of borane, in which the B atom has empty low-lying 2p orbitals, which easily accept electrons from the lone pair of a Lewis base, leading to a strong interaction usually known as a dative bond, which is nevertheless distinguished in the IUPAC's definition from a conventional covalent bond.[37] It is important to emphasize that strictly speaking, however, the difference between the interaction between a Lewis base and BH$_3$ and the interaction between a hydrogen-bond (HB) donor and an HB acceptor is only quantitative, in the sense that the charge transfer in the first case is much larger than in the second.

Actually, in very strong hydrogen bonds,[38−44] the charge donation from the HB acceptor to the HB donor is already rather significant. This charge transfer obviously implies a certain redistribution of the electron density of both interacting subunits, which in the case of an X—H···Y HB complex is reflected in the lengthening of the X—H bond of the proton donor. When dealing with BH$_3$ complexes, the interaction usually leads to a significant distortion of BH$_3$, which in the complex is not planar any more, but also in significant changes in the properties of the Lewis base.[45] For instance, when BH$_3$ interacts with phosphines to yield phosphine—boranes, both the physical and the chemical properties of the phosphine change.[46] Whereas the isolated phosphines have low stability and are pyrophoric, phosphine—boranes are rather stable solid compounds.[46] Also, whereas isolated phosphines are weak acids in the gas phase, phosphine—boranes exhibit an intrinsic acidity, which in terms of the acidity constant, is 17 orders of magnitude greater than that of the isolated phosphine, due to a much larger stabilization of the deprotonated than of the neutral phosphine upon complexation with BH$_3$.[46] Similar acidity enhancements were also reported for complexes involving Lewis bases other than phosphines[47] and BF$_3$ as Lewis acid.[48]

The aim of this study is to investigate, through the use of high-level ab initio and density functional approaches, what would be the effect of replacing BH$_3$ by AlH$_3$. In order to analyze this question we have selected, as suitable model

Table 1. G4-Calculated Acidity ($\Delta_{acid}G^0$, kJ mol^{-1}) and Acidity Enhancement ($\Delta\Delta_{acid}G^0$, kJ mol^{-1}) for R–PH$_2$ Phosphines and the Corresponding R–PH$_2$:AlH$_3$ Phosphine–Alanes and R–PH$_2$:BH$_3$ Phosphine–Boranes

R	$\Delta_{acid}G^0$			$\Delta\Delta_{acid}G^0$	
	RPH$_2$	RPH$_2$:AlH$_3$	RPH$_2$:BH$_3$	RPH$_2$:AlH$_3$	RPH$_2$:BH$_3$
H	1507.8 (1509.7 ± 2.1)[a]	1325.5	1378.1[b]	182.3	129.7[b]
CH$_3$	1533.6 (1530.0 ± 2.5)[c]	1359.3	1375.0 ± 2.5[d]	174.3	158.6[e]
c-C$_3$H$_5$	1512.7 (1510.0 ± 3.0)[c]	1352.1	1408.9 ± 2.8[d]	160.6	104.8[e]
C$_6$H$_5$	1457.6 (1457.3 ± 0.8)[c]	1324.6	1375.0 ± 2.5[d]	133.0	82.6[e]

[a]Experimental value taken from ref 66. [b]This work. G4-calculated value. [c]Experimental values taken from ref 46. [d]Experimental values corresponding to the phosphine–boranes analogues were taken from ref 46. These values show that the acidity enhancement is greater for the alane than for the borane derivatives. [e]Values taken from ref 46.

systems, three different R–PH$_2$ phosphines, where the R substituent represents three very different situations: an alkyl group (methyl), a saturated nonaromatic ring (c-C$_3$H$_5$), and an aromatic ring (phenyl), and for which both the intrinsic acidity of the isolated phosphines and that of the corresponding phosphine–boranes are known. To the aforementioned three phosphines we have added PH$_3$ as a good reference system and because PH$_3$AlH$_3$ may serve as a hydrogen storage system,[49] as is the case for other AlH$_3$ complexes with nitrogen bases.[50] It is worth mentioning that phosphine–alanes have also an interesting chemistry[51] and can act as catalysts in many chemical processes.[52]

COMPUTATIONAL DETAILS

To calculate the intrinsic acidity of the systems under investigation with reliable accuracy we have used the G4 composite ab initio theory.[53] This composite technique, based on B3LYP-optimized geometries, improves the performance of lower Gn formalisms, yielding final total energies effectively at the CCSD(T,full)/G3LargeXP + HF limit level, and provides very accurate estimates for a great variety of reaction enthalpies.[53] However, this theory is very time-consuming when trying to investigate larger systems to those considered in this work, so we have also decided to carry out an assessment of a cheaper theoretical model based on the use of the B3LYP density functional theory (DFT) approach.[54,55] This model has been shown to perform very well as far as the calculation of the intrinsic acidities of phosphine–boranes is concerned,[46] but its reliability when using heavier Lewis acids has not been investigated. In this model the geometries and the corresponding harmonic vibrational frequencies are obtained by using a 6-31+G(d,p) basis set, whereas the final energies are obtained by means of single-point calculations using a more extended 6-311+G(3df,2p) basis set expansion. Since aluminum is much larger than B we have explored also the performance of a functional including dispersion interactions, namely, B97D[56] as well as the M06 functional.[57] In both cases the basis sets used for geometry optimizations and to get the final energies were the same used for the B3LYP calculations. The calculated values obtained with these theoretical models are compared with those calculated at the G4 level of theory in Table S1 of the Supporting Information. It can be seen that, although the DFT models perform very well for the isolated phosphines, with differences below 4 kJ mol^{-1}, the performance is a little poorer for the phosphine–alanes, but still the correlation between the G4 and the B3LYP values is very good (see Figure S1 of the Supporting Information) indicating that the relative acidity trends are very well reproduced at the latter level.

The charge donation from the phosphorus lone pairs into AlH$_3$ empty orbitals, which constitutes the main ingredient in the bonding between phosphines and aluminum trihydride, will be analyzed in terms of the values of the orbital interaction energies obtained through a second-order perturbation approach in the framework of the natural bond orbital (NBO) method.[8] Using this same approach the population of the initially empty orbitals in the AlH$_3$ moiety will be also an interesting measurement of the strength of the interaction. This information will be complemented with the one obtained through two alternative partition techniques, namely, the atoms in molecules (AIM)[58] and the electron localization function (ELF) theories.[59,60] By means of the former we will be able to build up the molecular graph of each of the complexes formed as the ensemble of bond critical points (BCPs) and bond paths. The electron density associated to the P–Al BCP should be a good quantitative measurement of the strength of the linkage, but at the same time, the densities associated to the remaining bonds of the system will provide useful information on the electron density redistribution undergone by two interacting subunits upon complexation.[61,62] A similar but complementary information can be obtained by means of the ELF theory which permits the partition of the molecular space in regions associated with the probability of finding electron pairs, usually named monosynaptic and di- (or poly) synaptic basins, depending on the number of atomic valence shells participating in it. The electron population of the disynaptic basins located between two atoms of the system provides reliable information of the strength of the linkage between them. All the NBO calculations have been carried out with the NBO5G package,[63] whereas the AIM and ELF ones have been carried out with the AIMALL[64] and the TopMod[65] series of programs, respectively.

RESULTS AND DISCUSSION

The optimized geometries of the isolated phosphines and their phosphorus deprotonated anions, together with those of the complexes they formed with AlH$_3$, are given in Table S2 of the Supporting Information. The G4 and B3LYP/6-311+G(3df,2p) final energies are summarized in Table S3 of the Supporting Information. The calculated intrinsic acidities, measured as the Gibbs free energy associated with the reaction
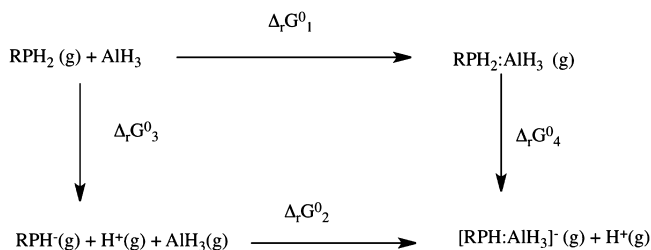
$$AH \rightarrow A^- + H^+ \tag{1}$$

are presented in Table 1.

As also found for phosphine–boranes,[46] the phosphine–alanes behave as phosphorus acids in the gas phase. For example, for the CH$_3$PH$_2$:AlH$_3$ adduct, the C–H deprotonation and the Al–H deprotonation processes are 138 and 201 kJ mol^{-1}, respectively, less favorable than the P–H deprotonation.

The first conspicuous fact is the significant increase of the acidity of the phosphine when the aluminum trihydride molecule is attached to the phosphorus atom. Interestingly,

this enhancement is larger than the one reported for the corresponding phosphine−borane complexes.[46] Similar to what was found for phosphine−boranes, this acidity enhancement points out to a different stabilization of the neutral and the deprotonated species, which are related with the corresponding intrinsic acidities through the thermodynamic cycle shown in Scheme 1.

Scheme 1

$$RPH_2 (g) + AlH_3 \xrightarrow{\Delta_r G^0_1} RPH_2:AlH_3 \ (g)$$

$$\downarrow \Delta_r G^0_3 \qquad\qquad \downarrow \Delta_r G^0_4$$

$$RPH^- (g) + H^+ (g) + AlH_3 (g) \xrightarrow{\Delta_r G^0_2} [RPH:AlH_3]^- (g) + H^+ (g)$$

In this scheme, $\Delta_r G^0_3$ and $\Delta_r G^0_4$, define the intrinsic acidity of the isolated phosphine and that of the phosphine:AlH$_3$ complex, respectively, assuming, as is the case, that in both cases the proton is lost from the PH$_2$ group. These free energies have been called generically $\Delta_{acid} G^0$ in Table 1. Hence, $\Delta_r G^0_1$ and $\Delta_r G^0_2$ measure the stabilization of the neutral phosphine and that of its deprotonated species, respectively, upon complexation with AlH$_3$. Accordingly, the aforementioned acidity enhancement just indicates that $\Delta_r G^0_2$ clearly dominates over $\Delta_r G^0_1$. In other words, that the stabilization of the anionic species is significantly higher than the stabilization undergone by the neutral phosphine, as is indeed the case as shown in Table 2.

Table 2. Stabilization Free Energies of Neutral ($\Delta_r G^0_1$) and Deprotonated ($\Delta_r G^0_2$) Phosphines, RPH$_2$, upon AlH$_3$ and BH$_3$ Complexation[a,b]

R	$\Delta_r G^0_1$		$\Delta_r G^0_2$	
	RPH$_2$:AlH$_3$	RPH$_2$:BH$_3$	RPH$_2$:AlH$_3$	RPH$_2$:BH$_3$
H	−23.2	−51	−205.5	−180
CH$_3$	−43.3	−56	−217.6	−176
c-C$_3$H$_5$	−42.6	−56	−203.2	−163
C$_6$H$_5$	−37.1	−50	−170.1	−129

[a]Values for the complexation with BH$_3$ taken from ref 46, except for R = H which corresponds to the G4 calculations of this work. [b]All values are in kJ mol^{-1}.

Quite unexpected, however, the acidity enhancement predicted for the phosphine−alanes is significantly larger, as clearly shown in Table 1, than that measured for the phosphine−boranes. On the other hand this acidity enhancement depends on the nature of the substituent and is significantly larger for R = CH$_3$ or c-propyl than for R = Ph.

These results open the following questions: why is the interaction of AlH$_3$ larger for the deprotonated than for the neutral species, why does this effect depend significantly on the nature of the R substituent, and why is the effect on the intrinsic acidities larger than that observed upon complexation with BH$_3$?

It is apparent from the electron densities at the P−Al BCPs (see Figure 1) that these bonds are much stronger in the anionic than in the neutral systems, which seems to indicate
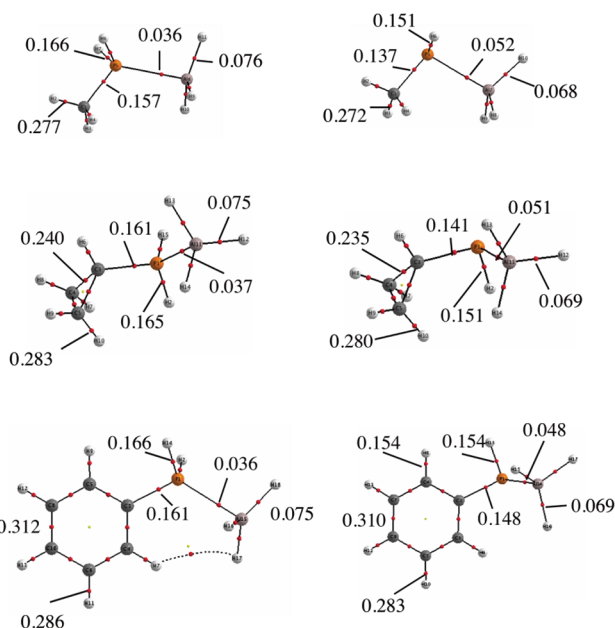

Figure 1. Molecular graphs of phosphine−alanes and their P deprotonated species. Red dots denote the BCPs. Electron densities are in au.

that the deprotonated anionic form is a better electron donor than the corresponding neutral phosphine. This is not surprising since the formation of the anion triggers a significant increase of the orbital energies, and in particular in the energy of the highest occupied molecular orbital (HOMO).

This change on going from the neutral to the deprotonated species is nicely reflected in the NBO characteristics of the P−Al bond (see Table 3). In the anion, the contribution of the Al

Table 3. Characteristics of the P−Al Bonds in Terms of the Percentage of Hybrid Orbitals Participating in Each MO and P−Al Wiberg Bond Index for Phosphine−Alanes and Their Deprotonated Forms[a]

system	P−Al bond	Wiberg bond index
CH$_3$PH$_2$:AlH$_3$	85% P (37% s + 62% p) + 15% Al (12% s + 86% p)	0.489
[CH$_3$PH]$^-$:AlH$_3$	76% P (23% s + 77% p) + 24% Al (22% s + 78% p)	0.728
c-propyl-PH$_2$:AlH$_3$	85% P (36% s + 64% p) + 15% Al (13% s + 87% p)	0.493
[c-propyl-PH]$^-$:AlH$_3$	76% P (22% s + 78% p) + 24% Al (22% s + 78% p)	0.726
PhPH$_2$:AlH$_3$	P (LP) → Al (3p) 426 kJ mol^{-1}	0.488
[PhPH]$^-$:AlH$_3$	77% P (17% s + 83% p) + 23% Al (22% s + 78% p)	0.675

[a]For PhPH$_2$:AlH$_3$ the NBO method does not localize any P−Al bond. Instead a strong charge donation from the P lone pair into the 3p empty orbital of Al is found. The corresponding interaction energy is included.

hybrids to the bond increase from about 15% to 24%, with a similar increase in the contribution of the 3s orbital with respect to the 3p orbital in the corresponding hybrid. Not surprisingly then, the Wiberg bond index[67] for the P−Al linkage is about 45% larger for the anion than for the neutral species (see Table 3).

It is important to note that, as shown in Table 2, $\Delta_r G^0_1$ is not very sensitive to the nature of the substituent, which means that most of acidity enhancement is associated to the effects on the values of $\Delta_r G^0_2$. Hence, to understand why the acidity enhancement depends on the nature of the R substituent we will concentrate our attention on the deprotonated species. The clue to understand why the smallest effect is observed for R = Ph is to notice that phenylphosphine is the stronger acid of the three phosphines considered. This is the result of the significant stabilization of the anion through the conjugation of the P lone pair, created in the deprotonation process, with the aromatic system. The complexation of the anion with AlH_3 necessarily competes with this delocalization, since a significant amount of the lone-pair charge is transferred to the alane molecule, and less is available for the conjugation with the aromatic ring. This is mirrored in a significant decrease (about 120 kJ mol^{-1}) in the second-order interaction energies between the P lone pair and the aromatic system, on going from PhPH$^-$ to PhPH$^-$:AlH$_3$.

The greater acidity enhancement effect observed for alane with respect to borane complexes is in principle unexpected if one takes into account that BH_3 should behave as a better Lewis acid than AlH_3. In fact, the dissociation energies of the complexes of AlH_3 with PF_3, PCl_3, PMe_3, and $P(CN)_3$ were reported to be smaller than for the analogous complexes in which AlH_3 is replaced by BH_3.[68] Indeed, this is also observed when looking at the stabilization of the neutral phosphines ($\Delta_r G^0_1$) under investigation here (see Table 2). Why, however, is the stabilization of the anion greater when it donates to AlH_3 than when it does so to BH_3 (see Table 2)? The explanation is nicely visualized in the corresponding ELF plots (see Figure 2).

In this figure we compare the ELF of CH_3PH_2:BH_3 and its phosphorus deprotonated species with those of CH_3PH_2:AlH_3 and its phosphorus deprotonated species. It is apparent that the differences are very tiny when comparing the corresponding neutral complexes. However, likely due to the larger size of the Al orbitals, there is a clear delocalization of the lone pair created

on the P atom upon its deprotonation and the disynaptic P–Al basin, which is not observed in the case of the phosphine–borane. This electron delocalization results in an increase electron flux to the bonding region, which is reflected in an increase of the electron population of the P–Al disynaptic basin, which would explain the enhanced stability of the $[CH_3PHAlH_3]^-$ with respect to that of the $[CH_3PHBH_3]^-$ counterpart and, therefore, the larger acidity of the phosphine–alane. The same delocalization is observed for the other derivatives as illustrated in the Figure S2 of the Supporting Information.

■ CONCLUSIONS

The association of phosphines RPH_2 (R = CH_3, c-C_3H_5, C_6H_5) with aluminum trihydride yields to very stable complexes which behave as much stronger acids than the isolated phosphines. This dramatic acidity enhancement, which can be as high as 174 kJ mol^{-1}, is due to the fact that the interaction of the deprotonated phosphine with AlH_3 is much stronger than that calculated for the neutral system. Actually, the deprotonation significantly increases the electron donor capacity of the phosphine moiety, whose HOMO becomes much higher in energy than that of the neutral compound. This effect depends quantitatively on the nature of the substituent R and is smaller for R = C_6H_5 because of the conjugation of the P lone pair with the aromatic system that cannot occur when R is an alkyl substituent. More unexpectedly, however, the phosphine–alane complexes, RPH_2:AlH_3, are more acidic than the corresponding phosphine–borane analogues, RPH_2:BH_3. This unexpected result is due to the enhanced stability of the anionic deprotonated species for complexes involving AlH_3, because a delocalization of the newly created P lone pair with the P–Al disynaptic basin is more favorable when the Lewis acid is aluminum trihydride than when it is borane.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Calculated acidities of phosphines and phosphine–alanes obtained at the G4 level and by using the B3LYP, M06, and B97D functionals; linear correlations between G4- and DFT-calculated acidities for phosphines and phosphine–alanes; B3LYP/6-31+G(d,p)-optimized geometries; G4 and B3LYP/6-311+G(3df,2p) total free energies for phosphines and phosphine–alanes; ELF plots for the RPH_2 (R = CH_3, c-C_3H_5, C_6H_5) phosphines and their complexes with AlH_3. This material is available free of charge via the Internet at http://pubs.acs.org.
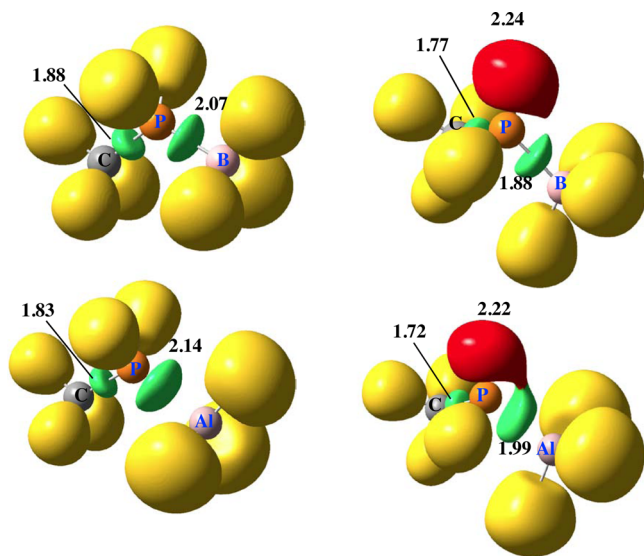
■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

Figure 2. ELF (= 0.85) for the CH_3PH_2:XH_3 (X = B, Al) complexes and their corresponding phosphorus deprotonated species, $[CH_3PH]^-$:XH_3 (X = B, Al). Green lobes denote disynaptic basins involving two heavy atoms. Yellow lobes are disynaptic basins in which H is one of the atoms involved. Red lobes correspond to lone pairs. The populations shown are in e$^-$.

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