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Article

Chemical Bonding in Phosphane and Amine Complexes of Main Group Elements and Transition Metals[†]

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The geometries and bond dissociation energies of the main group complexes $X_3B–NX_3$, $X_3B–PX_3$, $X_3Al–NX_3$, and $X_3Al–PX_3$ (X = H, Me, Cl) and the transition metal complexes $(CO)_5M–NX_3$ and $(CO)_5M–PX_3$ (M = Cr, Mo, W) have been calculated using gradient-corrected density functional theory at the BP86/TZ2P level. The nature of the donor–acceptor bonds was investigated with an energy decomposition analysis. It is found that the bond dissociation energy is not a good measure for the intrinsic strength of Lewis acidity and basicity because the preparation energies of the fragments may significantly change the trend of the bond strength. The interaction energies between the frozen fragments of the borane complexes are in most cases larger than the interaction energies of the alane complexes. The bond dissociation energy of the alane complexes is sometimes higher than that of the borane analogues because the energy for distorting the planar equilibrium geometry of BX_3 to the pyramidal from in the complexes is higher than for AlX_3. Inspection of the three energy terms, ΔE_{Pauli}, ΔE_{orb}, and ΔE_{elstat}, shows that all three of them must be considered to understand the trends of the Lewis acid and base strength. The orbital term of the donor–acceptor bonds with the Lewis bases NCl_3 and PCl_3 have a higher π character than the bonds of EH_3 and EMe_3, but NCl_3 and PCl_3 are weaker Lewis bases because the lone-pair orbital at the donor atoms N and P has a high percent s character. The calculated ΔE_{int} values suggest that the trends of the intrinsic Lewis bases' strengths in the main-group complexes with BX_3 and AlX_3 are $NMe_3 > NH_3 > NCl_3$ and $PMe_3 > PH_3 > PCl_3$. The transition metal complexes exhibit a somewhat different order with $NH_3 > NMe_3 > NCl_3$ and $PMe_3 > PH_3 > PCl_3$. The slightly weaker bonding of NMe_3 than that of NH_3 comes from stronger Pauli repulsion. The bond length does not always correlate with the bond dissociation energy, nor does it always correlate with the intrinsic interaction energy.

Introduction

Phosphanes and amines are probably the most commonly used ligands for complexes of transition metals and main group elements. The choice of the substituents, R, in the versatile bases NR_3 and PR_3 allows fine-tuning of the electronic and steric effects of the ligands which can be used to adjust the properties of the donor−acceptor complexes. The ubiquitous presence of amines and phosphanes comes also from their rather high donor strength which gives rise to stable complexes. Another advantage is that multidentate bases may be used, which enlarges the chances for tuning the chemical behavior of the complexes. Numerous representatives of phosphane and amine complexes are employed as powerful catalysts in homolytically catalyzed chemical reactions which are important for industrial purposes.[1]

The nature of the chemical bonding between a Lewis acid and the Lewis bases NR_3 and PR_3 has also been the subject of quantum theoretical studies.[2] Most studies were devoted to a particular class of complexes containing either amine or phosphane ligands.[3,4] We do not know about a theoretical work where the properties of amines and phosphanes in complexes of main group elements and transition metals are

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systematically studied and compared to each other. It is clearly desirable to have a deep understanding of the nature of the donor−acceptor interactions $A-NR_3$ and $A-PR_3$ (A = Lewis acid). The bonding is mostly discussed (i) in terms of electrostatic attraction between the lone-pair electrons of ER_3 (E = N, P) and the nucleus of the acceptor atom in A and (ii) using orbital interactions which mainly come from the $A \leftarrow ER_3$ σ donation of the lone-pair HOMO into the LUMO of A. The π back-donation $A \rightarrow ER_3$ is usually considered to be much weaker than the $A \leftarrow ER_3$ σ donation, but it may become important when electronegative R substituents yield low-lying empty π^* orbitals. The strength of the π back-donation in $(CO)_5Mo-PCl_3$ complexes was recently the topic of a controversy where different studies did not agree if PCl_3 is a weak or poor π acceptor.[2d,e,4j] We could show with the help of an energy decomposition analysis (EDA) that the $(CO)_5Mo \rightarrow PCl_3$ π back-donation is nearly as strong as $(CO)_5Mo \leftarrow PCl_3$ σ donation, but the strong back-donation is compensated by rather weak electrostatic attraction.[5a]

In this work, we report a systematic comparison of the nature of the bonding between amine and phosphane ligands and Lewis acids of main group elements and transition metals. We used the EDA which has proven to give deep insight into the nature of the chemical bond in a variety of donor−acceptor complexes[5] but also in molecules which have normal shared-electron bonds.[6] Other groups also employed the method for analyzing the nature of the chemical bond.[7] The EDA gives a quantitative estimate of the strength of electrostatic bonding and donor−acceptor bonding which can be separated into σ and π interactions. The molecules which were chosen for this work are the main group complexes between the Lewis acids BX_3 and AlX_3 and the Lewis bases NX_3 and PX_3 (X = H, Cl, Me). The results for the amine borane complexes are particularly interesting because of the relevance of the compounds for potential hydrogen storage.[8] For the transition metal complexes, we used the same Lewis bases NX_3 and PX_3 in the adducts $(CO)_5M-NX_3$ and $(CO)_5M-PX_3$ (M = Cr, Mo, W).

Methods

The calculations were performed at the nonlocal DFT level of theory using the exchange functional of Becke[9] and the correlation functional of Perdew[10] (BP86). Scalar relativistic effects were

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considered using the zero-order regular approximation (ZORA).[11] Uncontracted Slater-type orbitals (STOs) were used as basis functions for the SCF calculations.[12] Triple-ζ basis sets augmented by two sets of polarization functions were used for all atoms. This basis set is denoted as TZ2P. The $(n-1)s^2$ and $(n-1)p^6$ core electrons of the main group elements and the $(n-1)s^2$, $(n-1)p^6$, $(n-1)s^2$, and $(n-1)d^{10}$ core electrons of the transition metals were treated by the frozen-core approximation.[13] An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle.[14] The calculations were carried out with the program package ADF2.3.[15] The molecular geometries were optimized with C_s symmetry. To determine if the optimized structures are mimima on the potential energy surface, we calculated the vibrational frequencies of the stationary points. The frequency calculations were carried out at BP86 with our standard basis set II[16] which has valence-shell DZP quality using BP86/II-optimized geometries, which were found to be very similar to the BP86/TZ2P data.[17] This was done with the program package Gaussian 98,[18] which has analytical second derivatives.

The bonding interactions between the Lewis acids and bases were analyzed with the EDA method developed by Ziegler and Rauk[19] which is similar to the energy partitioning scheme of Morokuma.[20] The bond dissociation energy ΔE $(= -D_e)$ between two fragments A and B (in the this case, Lewis acid and base) is partitioned into several contributions which can be identified as physically meaningful entities. First, ΔE is separated into two major components ΔE_{prep} and ΔE_{int}

$$\Delta E\ (= -D_e) = \Delta E_{\text{prep}} + \Delta E_{\text{int}} \tag{1}$$

ΔE_{prep} is the energy necessary to promote fragments A and B from their equilibrium geometry and electronic ground state to the geometry and electronic state in the compound AB. ΔE_{int} is the instantaneous interaction energy between the two fragments in the molecule. The latter quantity will be part of the focus of the present work. The interaction energy ΔE_{int} can be divided into three main components

$$\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}} \tag{2}$$

ΔE_{elstat} gives the electrostatic interaction energy between the fragments which is calculated with the frozen electron density distribution of A and B in the geometry of the complex AB. The second term in eq 2, ΔE_{Pauli}, gives the repulsive interactions between the fragments, which are the result of two electrons with the same spin being unable to occupy the same region in space. The term comprises the four-electron destabilizing interactions between occupied orbitals. ΔE_{Pauli} is calculated by enforcing the Kohn–Sham determinant of AB, which results from superimposing fragments A and B, to obey the Pauli principle by antisymmetrization and renormalization. The stabilizing orbital interaction term, ΔE_{orb}, is calculated in the final step of the EDA when the Kohn–Sham orbitals relax to their optimal form. The latter term can be further partitioned into the contributions of the orbitals which belong to different irreducible representations of the interacting system. Further details about the method can be found in the literature.[15]

The EDA calculations of the main group complexes $X_3E{-}NX_3$ and $X_3E{-}PX_3$ (E = B, Al) was carried out using C_{3v} symmetry which gives orbital contributions with the symmetry a_1 (σ), a_2 (δ), and e (π). The transition metal complexes $(CO)_5M{-}NX_3$ and $(CO)_5M{-}PX_3$ have C_s symmetry which give a′ and a″ orbitals. Thus, one component of the degenerate $(CO)_5M{-}PX_3$ π-orbital interactions is part of the a″ term. To give the full strength of the π-orbital interactions, we calculated $\Delta E_\pi = 2 \times \Delta E_{\text{orb}}(a'')$ and $\Delta E_\sigma = \Delta E_{\text{orb}}(a') - \Delta E_{\text{orb}}(a'')$. The small deviations of the π-orbital strength from degenerate contributions can be neglected.

Borane and Alane Complexes $X_3B{-}NX_3$, $X_3B{-}PX_3$, $X_3Al{-}NX_3$, and $X_3Al{-}PX_3$ (X = H, Me, Cl)

Table 1 shows the EDA results and the most important bond lengths and bond angles for the borane–amine complexes $X_3B{-}NX_3$ (X = H, Cl, Me). The complete geometries and total energies are given in the Supporting Information. We give the energy values with two digits, not because we think that the accuracy is so high but so that the numbers can be reproduced.

The calculated bond dissociation energies, D_e, for $X_3B{-}NH_3$ and $X_3B{-}NMe_3$ have the order $BH_3 > BCl_3 > BMe_3$. The complexes $Cl_3B{-}NCl_3$ and $Me_3B{-}NCl_3$ dissociate during the geometry optimization. The EDA calculation of the latter species was carried out using the frozen B–N bond length of $H_3B{-}NCl_3$, while the rest of the structures was optimized. The data in Table 1 show that the energy necessary to deform the fragments from their equilibrium structure to the geometry in the complexes is rather big. This comes mainly from the BX_3 moieties which have a strongly pyramidal form in $X_3B{-}NX_3$, while the free molecules are planar. Table 1 shows that the ΔE_{prep} values are particularly large for BCl_3: between 20.90 and 28.51 kcal/mol. The EDA data show that, without the very large ΔE_{prep} values, the $Cl_3B{-}NCl_3$ and $Me_3B{-}NCl_3$ complexes might have comparably short donor–acceptor bonds as $H_3B{-}NCl_3$. The intrinsic interaction energy ΔE_{int} in the former two complexes at r(B–N) = 1.624 Å is attractive.

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Table 1. Results of the EDA Analysis of $X_3B{-}NX_3$ at the BP86/TZ2P Level[a]

	BH_3NH_3	BCl_3NH_3	BMe_3NH_3
B−N	1.657	1.633	1.697
B−X	1.215	1.843	1.626
X−B−X	113.6	113.7	114.3
ΔE_{int}	−44.55	−41.34	−27.71
ΔE_{Pauli}	108.82	192.76	128.48
ΔE_{elstat}	−77.33 (50.4%)[b]	−120.46 (51.5%)[b]	−83.81 (53.7%)[b]
ΔE_{orb}	−76.04 (49.6%)[b]	−113.64 (48.50%)[b]	−72.37 (46.3%)[b]
ΔE_{σ} (a1)	−68.36 (89.9%)[c]	−102.17 (89.9%)[c]	−65.10 (89.9%)[c]
ΔE_{π} (e)	−7.68 (10.1%)[c]	−11.29 (9.9%)[c]	−7.08 (9.8%)[c]
ΔE_{δ} (a2)	0.00	−0.17	−0.19
ΔE_{prep}	12.72	21.50	15.05
	12.66 (BH_3)	21.25 (BCl_3)	14.94 (BMe_3)
	0.06 (NH_3)	0.25 (NH_3)	0.11(NH_3)
ΔE (= $-D_e$)	−31.83	−19.84	−12.66

	BH_3NMe_3	BCl_3NMe_3	BMe_3NMe_3
B−N	1.651	1.677	1.777
B−X	1.219	1.852	1.630
X−B−X	113.1	111.3	111.8
ΔE_{int}	−51.42	−52.19	−31.28
ΔE_{Pauli}	119.79	187.42	115.14
ΔE_{elstat}	−89.42 (52.2%)[b]	−123.74 (51.6%)[b]	−79.78 (54.5%)[b]
ΔE_{orb}	−81.79 (47.8%)[b]	−115.86 (48.4%)[b]	−66.64 (45.5%)[b]
ΔE_{σ} (a1)	−71.06 (86.9%)[c]	−99.26 (85.7%)[c]	−57. 56 (86.4%)[c]
ΔE_{π} (e)	−10.68 (13.0%)[c]	−15.82 (13.7%)[c]	−8.46 (12.7%)[c]
ΔE_{δ} (a2)	−0.04	−0.79	−0.62
ΔE_{prep}	15.21	31.24	21.81
	13.78 (BH_3)	28.51 (BCl_3)	20.25 (BMe_3)
	1.43 (NMe_3)	2.73 (NMe_3)	1.56 (NMe_3)
ΔE (= $-D_e$)	−36.21	−20.95	−9.47

	BH_3NCl_3	BCl_3NCl_3	BMe_3NCl_3
B−N	1.624	1.624[d]	1.624[d]
B−X	1.209	1.829	1.627
X−B−X	115.3	113.3	113.1
ΔE_{int}	−23.14	−9.43	−10.30
ΔE_{Pauli}	108.01 (41.1%)[b]	186.43	142.70
ΔE_{elstat}	−53.92	−90.96 (46.4%)[b]	−69.22 (45.2%)[b]
ΔE_{orb}	−77.23 (58.9%)[b]	−104.90 (53.6%)[b]	−83.77 (54.8%)[b]
ΔE_{σ} (a_1)	−60.34 (78.1%)[c]	−84.10 (80.2%)[c]	−62.16 (74.2%)[c]
ΔE_{π} (e)	−16.86 (21.8%)[c]	−20.39 (19.7%)[c]	−21.31 (25.4%)[c]
ΔE_{δ} (a_2)	−0.03	−0.41	−0.30
ΔE_{prep}	9.16	20.99	17.11
	9.07 (BH_3)	20.90 (BCl_3)	15.93 (BMe_3)
	0.09 (NCl_3)	0.09 (NCl_3)	1.18 (NCl_3)
ΔE (= $-D_e$)	−13.98	11.56	6.81

[a] Interatomic distances, A−B, in angstroms, angles, A−B−C, in degreee; energies in kilocalories per mole. [b] Percentage of the total attractive interactions, $\Delta E_{elstat} + \Delta E_{orb}$. [c] Percentage of the orbital interactions, ΔE_{orb}. [d] Calculated with a frozen distance B−N, which was taken from BH_3NCl_3.

From the calculated energy data it becomes obvious that *the bond dissociation energy (BDE) is not a good measurement of the intrinsic donor−acceptor strength of the complexes*. For example, $H_3B{-}NMe_3$ has a much larger BDE (D_e = 36.21 kcal/mol) than $Cl_3B{-}NMe_3$ (D_e = 20.95 kcal/mol), but the latter complex has a slightly higher interaction energy (ΔE_{int} = −52.19 kcal/mol) than the former (ΔE_{int} = −51.42 kcal/mol). The ΔE_{int} values shown in Table 1 suggest that the intrisic strength of the Lewis acids BH_3 and BCl_3 at the equilibrium geometry of the complexes is similar to each other while BMe_3 is a weaker Lewis acid. Note that the equilibrium bond lengths of the $Me_3B{-}NX_3$ complexes are significantly longer than those of $H_3B{-}NX_3$ and $Cl_3B{-}NX_3$. From this, it might be concluded that the steric repulsion by the methyl groups weakens the inherent Lewis acid strength of BMe_3. The conclusion is not justified. The EDA data for $X_3B{-}NCl_3$, which have been calculated using the same distance for r(B−N) = 1.624 Å, show that the steric repulsion given by the ΔE_{Pauli} values is actually larger when X = Cl (ΔE_{Pauli} = 186.43 kcal/mol) than for X = Me (ΔE_{Pauli} = 142.70 kcal/mol). For the intrinsic Lewis base strength of the amines, the ΔE_{int} values show the order $NMe_3 > NH_3 > NCl_3$.

An inspection of the EDA data in Table 1 indicates that the donor−acceptor bonds in $X_3B{-}NX_3$ have about equally strong contributions from the quasiclassical electrostatic attraction and orbital interactions except in $H_3B{-}NCl_3$ where the orbital term contributes 59% to the total attractive interactions. The ΔE_{orb} values are otherwise slightly smaller than ΔE_{elstat}, but the differences are not very large. The breakdown of the ΔE_{orb} values into contributions from σ and π orbitals shows that the former are much larger than the latter. We want to point out that the absolute strength of ΔE_{π} in the $Cl_3B{-}NX_3$ equilibrium structures is as expected to be larger than that in the $H_3B{-}NX_3$ and $Me_3B{-}NX_3$. The *relative* contributions of the π-orbital interactions to ΔE_{orb} remains nearly the same, however. This is because the σ-orbital interactions in the latter complexes are also larger than in the former. The largest π character is found in $H_3B{-}NCl_3$ where ΔE_{π} contributes 21.8% to ΔE_{orb}. The energy contributions to the donor−acceptor bond in $Cl_3B{-}NCl_3$ and $Me_3B{-}NCl_3$ are not be discussed because they come from structures which are not energy minima. The very small orbital contributions from the ΔE_{δ} (a_2) term, coming from the polarization functions, are negligible. We want to point out, however, that the $H_3B{-}NCl_3$ bond has a significantly smaller contribution from the electrostatic attraction than the other $H_3B{-}NX_3$ complexes at their equilibrium geometry while the orbital interaction has a comparable strength. Table 1 shows that the ΔE_{orb} value of $H_3B{-}NCl_3$ (−77.23 kcal/mol) is slightly smaller than in $H_3B{-}NMe_3$ (−81.79 kcal/mol), and it is even stronger than in $H_3B{-}NH_3$ (−76.04 kcal/mol). It is the much smaller ΔE_{elstat} value that is responsible for the weaker bonding in $H_3B{-}NCl_3$. The electronegative chlorine atoms make the lone-pair orbital at nitrogen in NCl_3 much more compact than in NH_3 and NMe_3. The NBO analysis[21] showed that the percent s character of the nitrogen lone-pair in NCl_3 is 73.9%, while it is 27.3% in NH_3 and 16.5% in NMe_3.[17]

The EDA values for the borane−phosphane complexes $X_3B{-}PX_3$ (X = H, Cl, Me) are shown in Table 2. A comparison with the borane−amine analogues shows interesting differences. The theoretically predicted bond dissociation energies of $X_3B{-}PH_3$ are clearly smaller than those of $X_3B{-}NH_3$, particularly for X = Cl, Me. By contrast, the BX_3 complexes of PMe_3 and PCl_3 have larger D_e values than the respective complexes with NMe_3 and NCl_3. Note that the adducts $Cl_3B{-}PCl_3$ and $Me_3B{-}PCl_3$ are weakly bonded minima on the potential energy surface at BP86/TZ2P, while $Cl_3B{-}NCl_3$ and $Me_3B{-}NCl_3$ dissociate during the geometry optimization. The complex $H_3B{-}PMe_3$ has the largest bond

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(21) Reed, A. E.; Weinhold, F.; Curtiss, F. *Chem. Rev.* **1985**, *88*, 899.

Table 2. Results of the EDA Analysis of X_3B-PX_3 at the BP86/TZ2P Level[a]

	BH_3PH_3	BCl_3PH_3	BMe_3PH_3
B−P	1.939	2.026	2.070
B−X	1.213	1.838	1.627
X−B−X	114.7	114.4	114.8
ΔE_{int}	−38.58	−25.14	−14.72
$\Delta E_{\mathrm{Pauli}}$	113.29	166.36	112.14
$\Delta E_{\mathrm{elstat}}$	−57.95 (38.2%)[b]	−89.75 (46.1%)[b]	−59.43 (46.8%)[b]
ΔE_{orb}	−93.92 (61.8%)[b]	−104.74 (53.80%)[b]	−67.44 (53.2%)[b]
ΔE_{σ} (a_1)	−79.27 (84.6%)[c]	−92.00 (87.8%)[c]	−56.94 (84.4%)[c]
ΔE_{π} (e)	−14.65 (15.6%)[c]	−12.64 (12.1%)[c]	−10.42 (15.5%)[c]
ΔE_{δ} (a_2)	0.00	−0.10	−0.08
ΔE_{prep}	12.23	22.97	13.65
	10.42 (BH_3)	18.90 (BCl_3)	12.31 (BMe_3)
	1.81 (PH_3)	4.07 (PH_3)	1.34 (PH_3)
ΔE ($= -D_e$)	−26.35	−2.17	−1.07

	BH_3PMe_3	BCl_3PMe_3	BMe_3PMe_3
B−P	1.924	1.986	2.014
B−X	1.218	1.857	1.638
X−B−X	113.4	112.7	112.9
ΔE_{int}	−55.28	−52.73	−32.05
$\Delta E_{\mathrm{Pauli}}$	130.73	201.19	139.94
$\Delta E_{\mathrm{elstat}}$	−79.38 (42.7%)[b]	−121.81 (48.0%)[b]	−84.70 (49.2%)[b]
ΔE_{orb}	−106.63 (57.3%)[b]	−132.11 (52.0%)[b]	−87.29 (50.8%)[b]
ΔE_{σ} (a_1)	−92.72 (86.9%)[c]	−119.04 (90.1%)[c]	−76.05 (87.1%)[c]
ΔE_{π} (e)	−13.93 (13.0%)[c]	−12.81 (9.7%)[c]	−11.03 (12.6%)[c]
ΔE_{δ} (a_2)	−0.02	−0.26	−0.21
ΔE_{prep}	15.52	31.44	20.09
	13.16 (BH_3)	25.26 (BCl_3)	18.18 (BMe_3)
	2.36 (PMe_3)	6.18 (PMe_3)	1.91 (PMe_3)
ΔE ($= -D_e$)	−39.76	−21.29	−11.96

	BH_3PCl_3	BCl_3PCl_3	BMe_3PCl_3
B−P	1.909	2.166	2.110
B−X	1.211	1.810	1.618
X−B−X	116.2	116.3	116.3
ΔE_{int}	−30.75	−8.44	−6.79
$\Delta E_{\mathrm{Pauli}}$	112.36	109.72	94.04
$\Delta E_{\mathrm{elstat}}$	−48.70 (34.0%)[b]	−50.19 (42.5%)[b]	−44.01 (43.6%)[b]
ΔE_{orb}	−94.41 (66.0%)[b]	−67.97 (57.50%)[b]	−56.82 (56.4%)[b]
ΔE_{σ} (a_1)	−73.90 (78.3%)[c]	−56.19 (82.7%)[c]	−43.36 (76.3%)[c]
ΔE_{π} (e)	−20.51 (21.7%)[c]	−11.70 (17.2%)[c]	−13.36 (23.5%)[c]
ΔE_{δ} (a_2)	0.00	−0.09	−0.10
ΔE_{prep}	8.65	13.85	8.20
	7.32 (BH_3)	11.62 (BCl_3)	7.79 (BMe_3)
	1.33 (PCl_3)	2.23 (PCl_3)	0.41 (PCl_3)
ΔE ($= -D_e$)	−22.10	−5.41	−1.41

[a] Interatomic distances, A−B, in angstroms; angles, A−B−C, in degrees; energies in kilocalories per mole. [b] Percentage of the total attractive interactions, $\Delta E_{\mathrm{elstat}} + \Delta E_{\mathrm{orb}}$. [c] Percentage of the orbital interactions, ΔE_{orb}.

dissociation energy and also the largest ΔE_{int} value of all the borane complexes which have been studied by us, but it does not have the shortest B−P bond length. Table 2 shows that the H_3B-PCl_3 bond (1.909 Å) is shorter than the H_3B-PMe_3 bond (1.924 Å), but the former complex has clearly smaller values for D_e and ΔE_{int}. This is another example for the finding that bond length and bond strength do not always correlate with each other.[22]

The differences between the bond strength of the phosphane and amine complexes is not significantly influenced by the energy change of the fragments from the equilibrium form to the geometry in the complexes. Table 2 shows that the ΔE_{prep} values of the pairs of amine and phosphane complexes are very similar to each other. The energy which is necessary to pyramidalize the BX_3 fragments is in both cases the largest contributor to ΔE_{prep}. The ΔE_{int} values exhibit the same trend when the phosphane and the amine complexes are compared with each other. From this it follows that, with respect to boranes as Lewis acids, PH_3 is a weaker Lewis base than NH_3, while PMe_3 and PCl_3 are stronger Lewis bases than NMe_3 and NCl_3. The differences between the ΔE_{int} values of X_3B-PMe_3 and X_3B-NMe_3 are not very large, however. The intrinsic Lewis base strength of the phosphanes given by the interaction energies shows the order $PMe_3 > PH_3 > PCl_3$. Note that the bond dissociation energies do not reflect the trend of the intrinsic Lewis basicity because the preparation energies for some complexes are very large. The E_{int} values also suggest that the intrinsic Lewis acid strength of the boranes has the order $BH_3 > BCl_3 > BMe_3$. The latter order is not exactly the same as it found in the borane−amine complexes (Table 1), where the interaction energy in Cl_3B-NMe_3 is slightly higher (−52.19 kcal/mol) than in H_3B-NMe_3 (−51.42 kcal/mol). The data clearly show that the trend of the Lewis acid and Lewis base strength may depend on the bonding partner. The general trend for the boranes is $BH_3 \geq BCl_3 > BMe_3$.

The nature of the borane−phosphane bonds is not very different from that of the phosphane−amine bonds. The EDA results in Table 2 suggest that the phosphane complexes have a slighty higher covalent character given by the larger percentage contribution of ΔE_{orb} to the attractive interactions. The orbital interactions have only small contributions from π bonding which, have similar values to those of the amine complexes. The much weaker interaction energies of X_3B-PCl_3 than those of X_3B-PH_3 and X_3B-PMe_3 can be explained in the same manner as the borane−amine complexes with the significantly smaller contribution of the electrostatic term in the PCl_3 compounds. The lone-pair orbital at phosphorus in PCl_3 is much more compact than in PH_3 and PMe_3. The NBO analysis shows that the percent s(P) character in PCl_3 is 80.3%, while it is 56.7% in PH_3 and 55.1% in PMe_3.

The EDA results for the alane−amine complexes X_3Al-NX_3 are shown in Table 3. A review of experimentally known donor−acceptor complexes showed that $AlCl_3$ is a stronger Lewis acid than BCl_3 and that $Cl_3Al-NMe_3$ is the strongest-bonded donor−acceptor complex of main group elements.[2a] Table 3 shows that the Cl_3Al-NX_3 complexes indeed have larger D_e values than their respective Cl_3B-NX_3 species and that $Cl_3Al-NMe_3$ is the strongest-bonded adduct. However, the alane complexes have significantly smaller preparation energies, ΔE_{prep}, than the borane complexes. This is because AlX_3 needs much less energy than BX_3 to deform it from its planar equilibrium structure to the pyramidal geometry in the complexes. The EDA data in Tables 1 and 3 show that the intrinsic interaction energy, ΔE_{int}, between the frozen fragments in the borane complexes is higher than in the alane complexes. Thus, BCl_3 is intrinsically a stronger Lewis acid than $AlCl_3$. The same holds true for the group 13 hydrids. The interaction energies of the BH_3 complexes are much higher than the ΔE_{int} values of the AlH_3 complexes (Tables 1 and 3). But for the hydrid

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(22) Further examples are discussed in ref 2f.

Table 3. Results of the EDA Analysis of $X_3Al{-}NX_3$ at the BP86/TZ2P Level[a]

	AlH_3NH_3	$AlCl_3NH_3$	$AlMe_3NH_3$
Al−N	2.093	2.023	2.115
Al−X	1.611	2.129	1.996
X−Al−X	117.7	116.6	117.2
ΔE_{int}	−29.68	−39.46	−24.19
ΔE_{Pauli}	55.65	76.77	57.49
ΔE_{elstat}	−56.69 (66.4%)[b]	−75.92 (65.3%)[b]	−55.46 (67.9%)[b]
ΔE_{orb}	−28.65 (33.6%)[b]	−40.31 (34.70%)[b]	−26.22 (32.1%)[b]
ΔE_{σ} (a_1)	−24.43 (85.3%)[c]	−33.47 (83.0%)[c]	−22.26 (84.9%)[c]
ΔE_{π} (e)	−4.21 (14.7%)[c]	−6.77 (16.8%)[c]	−3.88 (14.8%)[c]
ΔE_{δ} (a_2)	0.00	−0.07	−0.09
ΔE_{prep}	3.43	6.26	4.08
	3.39 (AlH_3)	6.19 ($AlCl_3$)	4.05 ($AlMe_3$)
	0.04 (NH_3)	0.07 (NH_3)	0.03 (NH_3)
ΔE ($= -D_e$)	−26.25	−33.20	−20.11
	AlH_3NMe_3	$AlCl_3NMe_3$	$AlMe_3NMe_3$
Al−N	2.087	2.038	2.136
Al−X	1.615	2.139	2.001
X−Al−X	117.2	114.8	115.4
ΔE_{int}	−33.64	−46.14	−26.81
ΔE_{Pauli}	65.06	87.06	65.22
ΔE_{elstat}	−65.13 (66.2%)[b]	−84.81 (63.7%)[b]	−61.81 (67.2%)[b]
ΔE_{orb}	−33.39 (33.8%)[b]	−48.40 (36.3%)[b]	−30.22 (32.8%)[b]
ΔE_{σ} (a_1)	−26.15 (78.3%)[c]	−36.47 (75.3%)[c]	−23.65 (78.3%)[c]
ΔE_{π} (e)	−7.11 (21.3%)[c]	−11.43 (23.6%)[c]	−6.23 (20.6%)[c]
ΔE_{δ} (a_2)	−0.12	−0.50	−0.34
ΔE_{prep}	5.21	11.32	7.17
	4.21 (AlH_3)	9.60 ($AlCl_3$)	6.22 ($AlMe_3$)
	1.00 (NMe_3)	1.72 (NMe_3)	0.95 (NMe_3)
ΔE ($= -D_e$)	−28.43	−34.82	−19.64
	AlH_3NCl_3	$AlCl_3NCl_3$	$AlMe_3NCl_3$
Al−N	2.228	2.208	2.336
Al−X	1.602	2.111	1.984
X−Al−X	119.1	117.6	118.2
ΔE_{int}	−9.10	−12.24	−5.21
ΔE_{Pauli}	33.42	46.08	30.03
ΔE_{elstat}	−22.17 (52.1%)[b]	−29.85 (51.2%)[b]	−19.59 (55.6%)[b]
ΔE_{orb}	−20.35 (47.9%)[b]	−28.46 (48.80%)[b]	−15.65 (44.4%)[b]
ΔE_{σ} (a_1)	−15.43 (75.8%)[c]	−21.43 (75.3%)[c]	−11.92 (76.2%)[c]
ΔE_{π} (e)	−4.87 (24.0%)[c]	−6.88 (24.2%)[c]	−3.65 (23.4%)[c]
ΔE_{δ} (a_2)	−0.04	−0.15	−0.07
ΔE_{prep}	1.33	4.18	1.82
	1.22 (AlH_3)	4.04 ($AlCl_3$)	1.83 ($AlMe_3$)
	0.11 (NCl_3)	0.14 (NCl_3)	0.01 (NCl_3)
ΔE ($= -D_e$)	−7.77	−5.64	−3.39

[a] Interatomic distances, A−B, in angstroms; angles, A−B−C, in degrees; energies in kilocalories per mole. [b] Percentage of the total attractive interactions, $\Delta E_{elstat} + \Delta E_{orb}$. [c] Percentage of the orbital interactions, ΔE_{orb}.

complexes, the smaller preparation energy of the alane complexes was found to not compensate for the weaker interaction energies. The $H_3B{-}NX_3$ complexes have bigger values for ΔE_{int} and for D_e than those of the $H_3Al{-}NX_3$ adducts. In fact, the calculations predict that $H_3B{-}NMe_3$ has not only a higher bond dissociation energy than $H_3Al{-}NMe_3$, but its D_e value is even higher than that of $Cl_3Al{-}NMe_3$. The Lewis acid strength of BMe_3 and $AlMe_3$ is similar to that of the trichlorides. The $Me_3Al{-}NX_3$ complexes have slightly smaller ΔE_{int} values than their respective $Me_3B{-}NX_3$ species, but the smaller preparation energies of the aluminum compounds lead to higher D_e values than in the borane molecules. The ΔE_{int} values show that the Lewis acid strength of the alanes has the order $AlCl_3 > AlH_3 > AlMe_3$, while the Lewis base strength of the amines has the same order as in the borane complexes, $NMe_3 > NH_3 > NCl_3$. The weaker bonds of the NCl_3 complexes are caused by the significantly smaller contribution from the quasiclassical electrostatic attraction (Table 3).

There is a significant difference in the nature of the donor−acceptor interactions between the borane−amine complexes, $X_3B{-}NX_3$, and the alane analogues, $X_3Al{-}NX_3$. The relative contribution of the orbital term to the attractive interactions is clearly less in the latter species than in the former. The percentage values of ΔE_{orb} in $X_3Al{-}NH_3$ and $X_3Al{-}NMe_3$ are only ∼33%, while in $X_3B{-}NH_3$ and $X_3B{-}NMe_3$ they are ∼33%. The boron and aluminum complexes with the Lewis base NCl_3 have a higher covalent character, but the value for the aluminum adduct is also larger. The relative contribution of the π-orbital interactions to ΔE_{orb} is a little higher in the alane complexes, $X_3Al{-}NX_3$, than in the boron species, $X_3B{-}NX_3$, but the strongest contribution (>75%) still comes from the σ orbitals.

Table 4 gives the EDA results for the alane−phosphane complexes, $X_3Al{-}PX_3$. The bond dissociation energies, D_e, and the interaction energies, ΔE_{int}, are always smaller than for the alane−amine complexes (Table 3). This is different from the boron complexes where the adducts with PMe_3 and PCl_3 are more strongly bonded to the borane Lewis acids than the adducts with NMe_3 and NCl_3. The ΔE_{int} values in Tables 3 and 4 show that $AlCl_3$ is an intrinsically stronger Lewis acid than AlH_3. By contrast the Lewis acidity of BH_3 is nearly always stronger than that of BCl_3, except in the complexes with NMe_3 (Table 1), where the difference is very small. The intrinsic interaction energy in the alane−phosphane complexes (Table 4) is always smaller than in the boron−phosphane species (Table 2). Since the preparation energies of the former compounds are significantly less than in the latter species, some $X_3Al{-}PX_3$ complexes have larger BDE values than the respective $X_3B{-}PX_3$ compounds. The largest BDE is calculated for $Cl_3Al{-}PMe_3$ where $D_e = 30.01$ kcal/mol. The ΔE_{int} values show that the Lewis acid strength in $X_3Al{-}PX_3$ has the same order as in the alane−amine adducts (i.e., $AlCl_3 > AlH_3 > AlMe_3$), while the trend of the Lewis base strength is the same as in the borane complexes ($PMe_3 > PH_3 > PCl_3$). A comparison of the donor−acceptor strength between the borane and alane complexes shows that it is not possible to establish a trend for the Lewis acid and base strength which is independent from the bonding partner. The Lewis acid BH_3 has a stronger bond to PMe_3 than to NMe_3 which is revealed by the larger ΔE_{int} and D_e values (Tables 1 and 2). The Lewis base strength of the latter has the opposite order than it has when they are bonded to the Lewis acid AlH_3 (Tables 3 and 4).

An inspection of the energy contributions to the donor−acceptor interactions in $X_3Al{-}PX_3$ shows a significantly higher covalent bonding given by the percentage values of ΔE_{orb} than in the $X_3Al{-}NX_3$ bonds (Tables 3 and 4). The absolute values of the electrostatic term ΔE_{elstat} for the aluminum−phosphane complexes are always much smaller than for the aluminum−amine compounds, while the ΔE_{orb} values in the two classes of adducts remain nearly the same. The relative contributions of the π orbitals to ΔE_{orb} also remain quite small in $X_3Al{-}PX_3$. The weaker bonds in the

Table 4. Results of the EDA Analysis of $X_3Al{-}PX_3$ at the BP86/TZ2P Level[a]

	AlH_3PH_3	$AlCl_3PH_3$	$AlMe_3PH_3$
Al−P	2.560	2.520	2.648
Al−X	1.605	2.122	1.991
X−Al−X	118.8	117.2	118.2
ΔE_{int}	−16.36	−22.07	−10.21
ΔE_{Pauli}	39.57	55.05	35.60
ΔE_{elstat}	−28.63 (51.2%)[b]	−40.22 (52.1%)[b]	−25.45 (55.6%)[b]
ΔE_{orb}	−27.31 (48.8%)[b]	−36.90 (47.90%)[b]	−20.36 (44.4%)[b]
ΔE_{σ} (a_1)	−22.65 (82.9%)[c]	−31.56 (85.5%)[c]	−16.70 (82.0%)[c]
ΔE_{π} (e)	−4.66 (17.1%)[c]	−5.31 (14.4%)[c]	−3.63 (17.8%)[c]
ΔE_{δ} (a_2)	0.00	−0.03	−0.03
ΔE_{prep}	2.93	7.08	2.92
	1.80 (AlH_3)	4.93 ($AlCl_3$)	2.19 ($AlMe_3$)
	1.13 (PH_3)	2.15 (PH_3)	0.73 (PH_3)
ΔE (= $-D_e$)	−13.43	−14.99	−7.29

	AlH_3PMe_3	$AlCl_3PMe_3$	$AlMe_3PMe_3$
Al−P	2.488	2.444	2.540
Al−X	1.614	2.140	2.001
X−Al−X	117.4	115.4	116.6
ΔE_{int}	−29.92	−42.56	−22.16
ΔE_{Pauli}	56.57	76.75	55.14
ΔE_{elstat}	−50.16 (58.0%)[b]	−69.34 (58.1%)[b]	−47.33 (61.2%)[b]
ΔE_{orb}	−36.32 (42.0%)[b]	−49.98 (41.9%)[b]	−29.97 (38.8%)[b]
ΔE_{σ} (a_1)	−30.95 (86.9%)[c]	−42.99 (86.0%)[c]	−25.28 (84.3%)[c]
ΔE_{π} (e)	−5.35 (14.7%)[c]	−6.85 (17.2%)[c]	−4.60 (15.4%)[c]
ΔE_{δ} (a_2)	−0.02	−0.15	−0.09
ΔE_{prep}	5.90	12.55	6.36
	3.89 (AlH_3)	8.65 ($AlCl_3$)	4.79 ($AlMe_3$)
	2.01 (PMe_3)	3.90 (PMe_3)	1.57 (PMe_3)
ΔE (= $-D_e$)	−24.02	−30.01	−15.80

	AlH_3PCl_3	$AlCl_3PCl_3$	$AlMe_3PCl_3$
B−P	2.586	2.608	2.719
Al−X	1.602	2.110	1.985
X−Al−X	119.6	118.4	119.0
ΔE_{int}	−8.42	−10.22	−3.69
ΔE_{Pauli}	31.33	39.12	25.76
ΔE_{elstat}	−15.83 (39.8%)[b]	−20.33 (41.2%)[b]	−13.11 (44.5%)[b]
ΔE_{orb}	−23.92 (60.2%)[b]	−29.01 (58.80%)[b]	−16.35 (55.5%)[b]
ΔE_{σ} (a_1)	−18.12 (75.7%)[c]	−23.57 (81.2%)[c]	−12.15 (74.3%)[c]
ΔE_{π} (e)	−5.79 (24.2%)[c]	−5.40 (18.6%)[c]	−4.18 (25.6%)[c]
ΔE_{δ} (a_2)	−0.01	−0.04	−0.02
ΔE_{prep}	1.49	4.58	1.30
	0.57 (AlH_3)	2.74 ($AlCl_3$)	0.90 ($AlMe_3$)
	0.92 (PCl_3)	1.84 (PCl_3)	0.40 (PCl_3)
ΔE (= $-D_e$)	−6.93	−8.06	−2.39

[a] Interatomic distances, A−B, in angstroms; angles, A−B−C, in degrees; energies in kilocalories per mole. [b] Percentage of the total attractive interactions, $\Delta E_{elstat} + \Delta E_{orb}$. [c] Percentage of the orbital interactions, ΔE_{orb}.

PCl_3 complexes can again be explained by the significantly smaller contributions from the quasiclassical electrostatic attraction (Table 4).

The free Lewis acids BX_3 and AlX_3 have planar equilibrium geometries which become pyramidal in the amine and alane complexes. Figure 1 shows a correlation of the X−B−X and X−Al−X angles in the complexes with the calculated intrinsic interaction energy, ΔE_{int}. It becomes obvious that a stronger donor−acceptor interaction yields a smaller bond angle which indicates a more pyramidal geometry.

Transition Metal Complexes $(CO)_5M{-}NX_3$ and $(CO)_5M{-}PX_3$ (M = Cr, Mo, W; X = H, Me, Cl)

Table 5. Results of the EDA Analysis of $(CO)_5M{-}NX_3$ at the BP86/TZ2P Level[a]

	$Cr(CO)_5NH_3$	$Mo(CO)_5NH_3$	$W(CO)_5NH_3$
M−N	2.225	2.368	2.355
M−CO_{trans}	1.847	1.984	1.988
M−CO_{cis}	1.895	2.051	2.047
CO_{trans}−M−CO_{cis}	89.2	88.9	89.0
ΔE_{int}	−27.65	−28.01	−32.04
ΔE_{Pauli}	47.36	46.07	55.60
ΔE_{elstat}	−50.01 (66.7%)[b]	−50.58 (68.3%)[b]	−60.27 (68.8%)[b]
ΔE_{orb}	−25.00 (33.3%)[b]	−23.49 (31.7%)[b]	−27.36 (31.2%)[b]
ΔE (a′)	−22.97	−21.26	−24.80
ΔE (a″)	−2.03	−2.23	−2.56
ΔE_{σ}	−20.94 (83.8%)[c]	−19.03 (81.0%)[c]	−22.24 (81.3%)[c]
ΔE_{π}	−4.06 (16.2%)[c]	−4.46 (19.0%)[c]	−5.12 (18.7%)[c]
ΔE_{prep}	0.37	0.84	0.82
	0.36 ($Cr(CO)_5$)	0.83 ($Mo(CO)_5$)	0.81 ($W(CO)_5$)
	0.01 (NH_3)	0.01 (NH_3)	0.01 (NH_3)
ΔE (= $-D_e$)	−27.28	−27.19	−31.22

	$Cr(CO)_5NMe_3$	$Mo(CO)_5NMe_3$	$W(CO)_5NMe_3$
M−N	2.329	2.439	2.423
M−CO_{trans}	1.845	1.979	1.985
M−CO_{cis}	1.895	2.050	2.047
CO_{trans}−M−CO_{cis}	88.0	87.4	87.6
ΔE_{int}	−24.90	−26.10	−30.38
ΔE_{Pauli}	46.24	48.63	58.82
ΔE_{elstat}	−46.36 (65.2%)[b]	−50.39 (67.4%)[b]	−60.63 (68.0%)[b]
ΔE_{orb}	−24.75 (34.8%)[b]	−24.33 (32.6%)[b]	−28.56 (32.0%)[b]
ΔE (a′)	−21.39	−20.84	−24.56
ΔE (a″)	−3.35	−3.49	−4.00
ΔE_{σ}	−18.05 (72.9%)[c]	−17.35 (71.3%)[c]	−20.56 (72.0%)[c]
ΔE_{π}	−6.70 (27.1%)[c]	−6.98 (28.7%)[c]	−8.00 (28.0%)[c]
ΔE_{prep}	2.39	2.36	2.87
	0.96 ($Cr(CO)_5$)	1.05 ($Mo(CO)_5$)	1.38 ($W(CO)_5$)
	1.43 (NMe_3)	1.31 (NMe_3)	1.49 (NMe_3)
ΔE (= $-D_e$)	−22.51	−23.79	−27.51

	$Cr(CO)_5NCl_3$	$Mo(CO)_5NCl_3$	$W(CO)_5NCl_3$
M−N	2.299	2.428	2.356.
M−CO_{trans}	1.843	1.970	1.982
M−CO_{cis}	1.901	2.056	2.054
CO_{trans}−M−CO_{cis}	88.0	87.7	88.4
ΔE_{int}	−8.99	−9.72	−13.32
ΔE_{Pauli}	35.41	35.34	50.01
ΔE_{elstat}	−24.35 (54.8%)[b]	−24.72 (54.9%)[b]	−34.06 (53.8%)[b]
ΔE_{orb}	−20.05 (45.2%)[b]	−20.33 (45.1%)[b]	−29.26 (46.2%)[b]
ΔE (a′)	−16.03	−16.28	−23.14
ΔE (a″)	−4.01	−4.05	−6.12
ΔE_{σ}	−12.03 (60.0%)[c]	−12.23 (60.2%)[c]	−17.02 (58.2%)[c]
ΔE_{π}	−8.02 (40.0%)[c]	−8.10 (39.8%)[c]	−12.24 (41.8%)[c]
ΔE_{prep}	1.10	0.84	2.05
	0.65 ($Cr(CO)_5$)	0.48 ($Mo(CO)_5$)	1.09 ($W(CO)_5$)
	0.45 (NCl_3)	0.36 (NCl_3)	0.96 (NCl_3)
ΔE (= $-D_e$)	−7.89	−8.88	−11.27

[a] Interatomic distances, A−B, in angstroms; angles, A−B−C, in degrees; energies in kilocalories per mole. [b] Percentage of the total attractive interactions, $\Delta E_{elstat} + \Delta E_{orb}$. [c] Percentage of the orbital interactions, ΔE_{orb}.

The EDA results of the transition metal−amine complexes, $(CO)_5M{-}NX_3$, are shown in Table 5. The metal−amine bonds of the Cr and Mo complexes have similar bond energies, while the tungsten compounds have slightly stronger bonds. The bond dissociation energies of the NMe_3 ligand are ∼4 kcal/mol smaller than those of NH_3, while NCl_3 is significantly more weakly bonded. The preparation energies of the fragments are very small. They do not change the trend of the bond strength. Thus, the intrinsic binding energies of $(CO)_5M{-}NX_3$ show the order $NH_3 > NMe_3 > NCl_3$. This is different from the borane and alane complexes where the ΔE_{int} values have the order $NMe_3 > NH_3 > NCl_3$ (Tables 1 and 3). Inspection of the energy terms shows that the nature of the $(CO)_5M{-}NH_3$ bonds is not very different

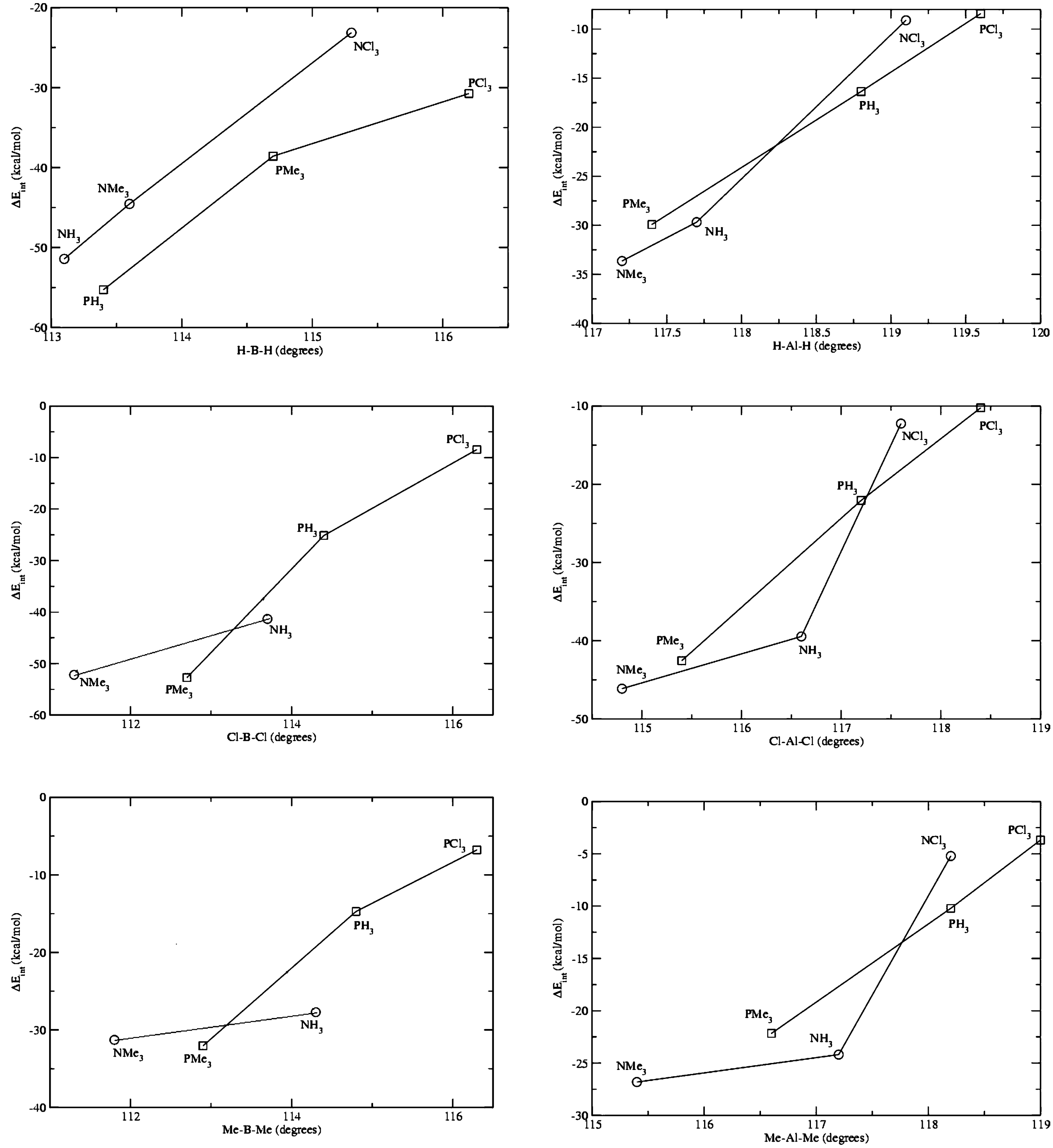

Figure 1. Correlation of the calculated interaction energy, ΔE_{int}, with the optimized bond angles X−B−X and X−Al−X.

from the nature of the $(CO)_5M-NMe_3$ bonds (Table 5). The quasiclassical electrostatic term contributes about two-thirds to the attractive interactions, and the orbital term contributes one-third. The $(CO)_5M-NMe_3$ bonds have a slightly higher π character than the $(CO)_5M-NH_3$ bonds, but this does not explain the weaker bond. An explanation can be given when the values for the Pauli repulsion are considered. The $(CO)_5M-NMe_3$ bonds are clearly longer than the $(CO)_5M-NH_3$ bonds, but the $\Delta E_{\mathrm{Pauli}}$ values of the latter compounds are only slightly smaller in the chromium compound or even larger in the molybdenum and tungsten species. The increase of the Pauli repulsion at shorter distances is in systems which have more than two electrons; the reason a chemical bond does not become shorter as its actual equilibrium value.[6a] The data in Table 5 suggest that the increase of $\Delta E_{\mathrm{pauli}}$ in $(CO)_5M-NMe_3$ compensates for the increase of the attractive interactions, $\Delta E_{\mathrm{elstat}}$ and ΔE_{orb}, at longer distances than in $(CO)_5M-NMe_3$. From this it follows that it is the Pauli repulsion in $(CO)_5M-NMe_3$ which prevents a shorter and stronger bond. The significantly weaker $(CO)_5M-NCl_3$

Table 6. Results of the EDA Analysis of $(CO)_5M{-}PX_3$ at BP86/TZ2P Level[a]

	$Cr(CO)_5PH_3$	$Mo(CO)_5PH_3$	$W(CO)_5PH_3$
M−P	2.352	2.530	2.514
$M{-}CO_{trans}$	1.866	2.012	2.014
$M{-}CO_{cis}$	1.894	2.053	2.051
$CO_{trans}{-}M{-}CO_{cis}$	90.2	89.7	90.0
ΔE_{int}	−33.28	−31.36	−36.32
ΔE_{Pauli}	82.77	70.56	86.49
ΔE_{elstat}	−65.56 (56.5%)[b]	−58.96 (57.8%)[b]	−72.98 (59.4%)[b]
ΔE_{orb}	−50.50 (43.5%)[b]	−42.97 (42.2%)[b]	−48.54 (40.4%)[b]
ΔE (a′)	−42.72	−35.68	−41.66
ΔE (a″)	−7.78	−7.28	−8.17
ΔE_σ	−34.94 (69.2%)[c]	−28.41 (66.1%)[c]	−33.49 (67.2%)[c]
ΔE_π	−15.56 (30.8%)[c]	−14.56 (33.9%)[c]	−16.34 (32.8%)[c]
ΔE_{prep}	1.36	1.94	2.26
	0.50 ($Cr(CO)_5$)	1.20 ($Mo(CO)_5$)	1.43 ($W(CO)_5$)
	0.86 (PH_3)	0.74 (PH_3)	0.83 (PH_3)
ΔE ($= -D_e$)	−31.92	−29.42	−34.06
	$Cr(CO)_5PMe_3$	$Mo(CO)_5PMe_3$	$W(CO)_5PMe_3$
M−P	2.396	2.558	2.556
$M{-}CO_{trans}$	1.864	2.015	2.015
$M{-}CO_{cis}$	1.887	2.049	2.047
$CO_{trans}{-}M{-}CO_{cis}$	90.4	90.3	90.2
ΔE_{int}	−43.16	−40.66	−46.33
ΔE_{Pauli}	93.41	84.12	98.67
ΔE_{elstat}	−82.94 (60.7%)[b]	−79.30 (63.5%)[b]	−94.20 (65.0%)[b]
ΔE_{orb}	−53.62 (39.3%)[b]	−45.48 (36.5%)[b]	−50.79 (35.0%)[b]
ΔE (a′)	−46.86	−39.16	−43.98
ΔE (a″)	−6.76	−6.32	−6.81
ΔE_σ	−40.10 (74.8%)[c]	−32.84 (72.2%)[c]	−37.17 (73.2%)[c]
ΔE_π	−13.52 (25.2%)[c]	−12.64 (27.8%)[c]	−13.62 (26.8%)[c]
ΔE_{prep}	1.65	2.30	2.69
	0.67 ($Cr(CO)_5$)	1.41 ($Mo(CO)_5$)	1.67 ($W(CO)_5$)
	0.98 (PMe_3)	0.89 (PMe_3)	1.02 (PMe_3)
ΔE ($= -D_e$)	−41.51	−38.36	−43.64
	$Cr(CO)_5PCl_3$	$Mo(CO)_5PCl_3$	$W(CO)_5PCl_3$
M−P	2.300	2.465	2.460
$M{-}CO_{trans}$	1.879	2.025	2.025
$M{-}CO_{cis}$	1.901	2.059	2.056
$CO_{trans}{-}M{-}CO_{cis}$	89.1	89.1	89.3
ΔE_{int}	−27.72	−26.06	−30.95
ΔE_{Pauli}	78.67	70.94	83.63
ΔE_{elstat}	−49.67 (46.7%)[b]	−45.25 (46.60%)[b]	−55.54 (48.5%)[b]
ΔE_{orb}	−56.72 (53.3%)[b]	−51.75 (53.4%)[b]	−59.06 (51.5%)[b]
ΔE (a′)	−43.63	−39.22	−45.28
ΔE (a″)	−13.09	−12.53	−13.78
ΔE_σ	−30.54 (53.8%)[c]	−26.69 (51.6%)[c]	−31.50 (53.3%)[c]
ΔE_π	−26.18 (46.2%)[c]	−25.06 (48.4%)[c]	−27.56 (46.7%)[c]
ΔE_{prep}	1.24	2.01	2.27
	0.96 ($Cr(CO)_5$)	1.79 ($Mo(CO)_5$)	1.01 ($W(CO)_5$)
	0.28 (PCl_3)	0.22 (PCl_3)	0.26 (PCl_3)
ΔE ($= -D_e$)	−26.48	−24.05	−28.68

[a] Interatomic distances, A−B, in angstroms; angles, A−B−C, in degrees; energies are given in kilocalories per mole. [b] Percentage of the total attractive interactions, $\Delta E_{elstat} + \Delta E_{orb}$. [c] Percentage of the orbital interactions, ΔE_{orb}.

bonds can be explained with the smaller electrostatic contribution to the bond which comes from the more compact nitrogen lone-pair orbital. The same effect is observed for the main group complexes which have NCl_3 as a Lewis base.

Table 6 gives the EDA results for the transition metal−phosphane complexes, $(CO)_5M{-}PX_3$. The data show that the phosphane ligands always have stronger metal−ligand bonds than the amine ligands. The $(CO)_5M{-}PX_3$ bonds have a higher covalent character than the $(CO)_5M{-}NX_3$ bonds; this is revealed by the percentage values for ΔE_{orb}. The π contribution to the orbital interaction in the $(CO)_5M{-}PH_3$ and $(CO)_5M{-}PCl_3$ bonds is significantly higher than that in the $(CO)_5M{-}NH_3$ and $(CO)_5M{-}NCl_3$ bonds. The π-bonding contribution is particularly large in the $(CO)_5M{-}PCl_3$ complexes where the ΔE_π term is nearly as strong as ΔE_σ. The net attractive bonding in the latter species is weaker than that in the other phosphane complexes, $(CO)_5M{-}PH_3$ and $(CO)_5M{-}PMe_3$, because the electrostatic attraction is much weaker.

It is difficult to single out a particular energy term as the cause for the stronger bonds of the phosphane ligands than the amine ligands because the electrostatic attraction and the orbital interaction are both stronger in the phosphane ligands, although the relative increase of ΔE_{orb} is higher.

Summary

The results of the energy decomposition analyses of the donor−acceptor complexes can be summarized as follows.

The bond dissociation energy of the donor−acceptor bond is not a good measurement for the intrinsic strength of the Lewis acids and bases because the preparation energies of the fragments may significantly change the trend of the bond strength. The interaction energies between the frozen fragments of the borane complexes are in most cases larger than the interaction energies of the alane complexes. The bond dissociation energy of the alane complexes is sometimes higher than that of the borane analogues because the energy for distorting the planar equilibrium geometry of BX_3 to the pyramidal from in the complexes is higher than for AlX_3. An inspection of the three energy terms, ΔE_{Pauli}, ΔE_{orb}, and ΔE_{elstat}, shows that all three of them must be considered to understand the trends of the Lewis acid and base strength. The orbital term of the donor−acceptor bonds with the Lewis bases NCl_3 and PCl_3 has a higher π character than the bonds of EH_3 and EMe_3, but NCl_3 and PCl_3 are weaker Lewis bases because the lone-pair orbital at the donor atoms N and P has a high percent s character. The calculated ΔE_{int} values suggest that the trends of the intrinsic Lewis basis strength in the main group complexes with BX_3 and AlX_3 are $NMe_3 > NH_3 > NCl_3$ and $PMe_3 > PH_3 > PCl_3$. The transition metal complexes exhibit a slightly different order with $NH_3 > NMe_3 > NCl_3$ and $PMe_3 > PH_3 > PCl_3$. The slightly weaker bonding of NMe_3 than that of NH_3 comes from a stronger Pauli repulsion. The bond length does not always correlate with the bond dissociation energy nor does it correlate with the intrinsic interaction energy.

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Supporting Information Available: Additional Gaussian and ADF data for the complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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