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The Lewis Basicity of Diaminocarbene – A Theoretical Study of Donor–Acceptor Complexes of $C(NH_2)_2$, NH_3 and CO with the Lewis Acids EF_3, ECl_3 (E = B, Al, Ga, In), TiF_4 and $TiCl_4$

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Quantum chemical calculations at the MP2 level using large valence basis sets up to TZ+2P quality have been carried out in order to predict the geometries and bond energies of the title compounds. The nature of the donor–acceptor bond has also been investigated. The calculations show clearly that diaminocarbenes are much stronger Lewis bases than amines. The complexation energies of $C(NH_2)_2$ have been calculated to be 14–27 kcal/mol higher than those of NH_3. The most strongly bonded complex is $Cl_3Al–C(NH_2)_2$, which has a theoretically predicted Al–C bond energy D_o = 59.1 kcal/mol. In all the complexes, the strength of the Lewis bases is $C(NH_2)_2 > NH_3 > CO$, but the ordering of Lewis acid strength of EX_3 depends on the coordinated Lewis base. TiF_4 and $TiCl_4$ have similar Lewis acidities as BF_3, but the titanium tetrahalides may bind one or two donor molecules with almost the same bond strength. The investigated donor–acceptor bonds have a high degree of ionic character. The largest covalent contributions are found for the diaminocarbene complexes. The covalent character of the $X_3E–CO$ bond increases on going from E = boron to the heavier Group 13 elements, while the opposite order is found for the $X_3E–NH_3$ and $X_3E–C(NH_2)_2$ bonds.

Introduction

The concept of “dative” or “semipolar” bonds between an electron-pair donor and an acceptor introduced by Lewis[1] has become very useful for understanding the structures, bond strengths, and reactivities of donor−acceptor complexes. Chemical bonding in main group chemistry is usually discussed in terms of covalent or ionic interactions and the model of donor−acceptor bonds plays only a minor role. In contrast, it is customary to consider chemical bonding in transition metal compounds as arising from closed-shell interactions between the metal M and the donor ligand D, even when formal cleavage of the M−D bond yields charged fragments M^+ and D^-. This is because coordination compounds are much more common in transition metal chemistry than in main group element chemistry. Nevertheless, it has been shown that the donor−acceptor model is a very useful device for many main group compounds as well.[2]

The strength of a donor−acceptor bond depends on the Lewis acidity and basicity of the binding partners. A given set of Lewis acids or bases can be classified in order of ascending acidity/basicity, but this order may only be valid with respect to a particular binding partner. For example, the π-donor ability of the halogens in BX_3 increases regularly on going from X = fluorine to iodine,[3] but the Lewis acid strength of BX_3 either increases or decreases on going from BF_3 to BI_3, depending on whether the donor−acceptor bond in the complex has more ionic or covalent character. This is the well-known basis of the model of hard and soft acids and bases.[4]

A Lewis base is characterized by having an energetically high-lying electron pair, which serves as the donor moiety. This can either be an atom-centered electron lone-pair, or the π-electrons of a multiple bond. Compounds that have neither lone-pair electrons nor multiple bonds[5] are usually weak Lewis bases. The strongest donor−acceptor bond of a main group complex that has been determined experimentally is that between NMe_3 and $AlCl_3$.[2] The measured dissociation energy of $Cl_3Al−NMe_3$ in the gas phase is D_o = 47.5 ± 2.0 kcal/mol.[6] Even stronger bonds have been predicted theoretically for donor−acceptor complexes of the strong Lewis acid BeO, but this has not yet been experimentally verified.[7]

It is generally the case that the Lewis basicity of lone-pair donor molecules increases on going from right to left across the periodic system of the elements. Thus, the trend in the donor strengths is Ne < FH < OH_2 < NH_3. The next member of this series would be ($^1A_1$) CH_2. Indeed, carbenes are well-known ligands in transition metal chemistry[8] and many transition metal carbene complexes have been synthesized and characterized since Fischer isolated the first example of such a species.[9] Main group carbene complexes have only been known following the isolation by Arduengo of the first stable carbene, i.e. the 1,3-bis(adamantyl) derivative of imidazol-2-ylidene **A** (Scheme 1).[10] Several complexes of substituted analogues of **A** with BH_3, BF_3, AlH_3, and other Lewis acids have since been synthesized.[11][12]

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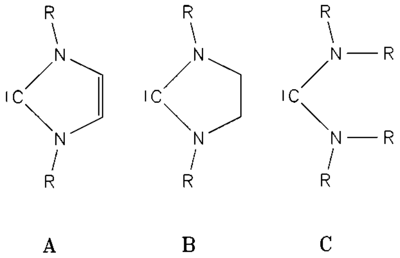


Scheme 1. Examples of diaminocarbenes that have been synthesized

The chemistry of *N*-heterocyclic carbenes has become one of the most extensively investigated areas of organic and organometallic chemistry in the last decade. Milestones were the isolation of stable saturated diaminocarbenes **B**,[13] the synthesis of stable noncyclic diaminocarbenes **C**,[14] and reports on stable heterocyclic carbenes with other neighbouring atoms such as sulfur[15][16] and oxygen.[16] The interest in metal complexes of *N*-heterocyclic carbenes increased considerably after it was reported that carbene complexes exhibit catalytic properties which might be comparable with those of phosphane complexes.[12][17] In spite of numerous experimental studies, there has been no report concerning the measurement of the bond strength of a donor−acceptor bond between a metal and an *N*-heterocyclic carbene ligand. Experimental observations indicate that the bonds are quite strong, and that the donor−acceptor bonds show mainly carbene→metal σ-donation but little carbene←metal π-back-donation.[12] This assumption is supported by two recent theoretical studies of carbene complexes with beryllium[18] and Group 11 transition metal halides (CuCl, AgCl, AuCl).[19]

The focus of the present paper is the trend in the donor strengths of Lewis bases on going from nitrogen to carbon, i.e. the difference between the donor−acceptor bond strengths of amines and *N*-heterocyclic carbenes when they are bonded to Lewis acids of main group elements or early transition metals. We have chosen the parent compounds NH_3 as the amine and $C(NH_2)_2$ as the carbene. CO has also been included in order to highlight the different donor abilities of carbon lone-pair electrons in sp- and sp^2-hybridized orbitals. The difference between the Lewis basicities of NH_3 and substituted amines is known from experimental[20] and theoretical work.[21] $C(NH_2)_2$ should be a good model for studying the donor strength of *N*-heterocyclic carbenes since substituents at nitrogen influence the carbene center only indirectly. The different donor abilities of $C(NH_2)_2$ and substituted analogues thereof is the subject of another ongoing study in our group. The chosen Lewis acids were the main group compounds EF_3, ECl_3 (E = B, Al, Ga, In) and the titanium tetrahalides TiF_4 and $TiCl_4$. We report here the equilibrium geometries and bond energies calculated at the MP2 level using polarized valence basis sets of up to TZ+2P quality. The electronic structures of the molecules were analyzed with the help of the natural bond orbital (NBO) partitioning scheme developed by Weinhold.[22] This work is part of our ongoing systematic investigation of the structures and stabilities of donor−acceptor complexes of main group and transition metal elements.[23]

Theoretical Methods

The geometry optimizations were carried out using Møller−Plesset perturbation theory terminated at second order (MP2)[24] in conjunction with our standard basis set II,[25] which has a relativistic effective core potential (ECP)[26] with a (441/2111/41) valence basis set for Ti, 6−31G(d)[27] all-electron basis sets for H, B, C, N, O, and F, and ECPs with a (31/31/1) valence basis set for the heavier main-group elements Al, Ga, In, Cl.[28] Improved energy calculations were carried out at the MP2 level using the larger basis set II+. The latter has an additional f-type polarization function at Ti ($\zeta = 1.506$),[29] 6−311G(2d,p)[30] all-electron basis sets for H, B, C, N, O, F, Al, and Cl, and ECPs with a TZ+2P valence basis set (311/311/11)[28] for Ga and In. The harmonic vibrational frequencies and zero-point vibrational energies (*ZPE*) were calculated at the MP2/II level. All structures reported here are minima on the potential energy surface (only positive eigenvalues of the Hessian matrix). The calculations were carried out using the Gaussian-94 program package.[31]

Bond Energies and Geometries

Figure 1 shows the optimized structures and the most important geometrical parameters predicted at the MP2/II level of theory for the complexes **1a**−**10cc** comprising the Lewis acids **1**−**10** and the Lewis bases **a**−**c**. Table 1 gives the energies calculated at the MP2/II+ level using the MP2/II optimized geometries.

The calculated bond dissociation energies of the main group and transition metal complexes containing $C(NH_2)_2$ are very high, showing that the diaminocarbene ligand is a very strong Lewis base. The largest value is calculated for $Cl_3Al-C(NH_2)_2$ (**6c**) (D_e = 61.6 kcal/mol; D_o = 59.1 kcal/mol), while the lowest is predicted for $F_4Ti-C(NH_2)_2$ (**9c**) (D_e = 38.5 kcal/mol). Thus, diaminocarbenes are not only stronger Lewis bases than NH_3, but are even stronger than $N(CH_3)_3$, for which a bond dissociation energy of D_e = 50.2 kcal/mol (D_o = 47.6 kcal/mol, experimental value D_o = 47.5 ± 2 kcal/mol)[6] has been predicted at the MP2/II level for the complex $Cl_3Al-N(CH_3)_3$.[23b] It can thus be foreseen that complexes between *N*-heterocyclic carbenes and $AlCl_3$ will soon replace $Cl_3Al-N(CH_3)_3$ as the most strongly bonded donor−acceptor complexes of main group elements known experimentally.

The Lewis basicity of NH_3 is also high, but is clearly lower than that of $C(NH_2)_2$. The bond dissociation energies of the ammonia complexes are calculated to be between D_e = 44.1 kcal/mol (Cl_3Al-NH_3, **6a**) and D_e = 24.1 kcal/mol (F_4Ti-NH_3 **9a**) for complexes with one Lewis base. The second ammonia ligand in $F_4Ti(NH_3)_2$ (**9aa**) has the lowest bond energy among the NH_3 complexes (D_e = 21.6

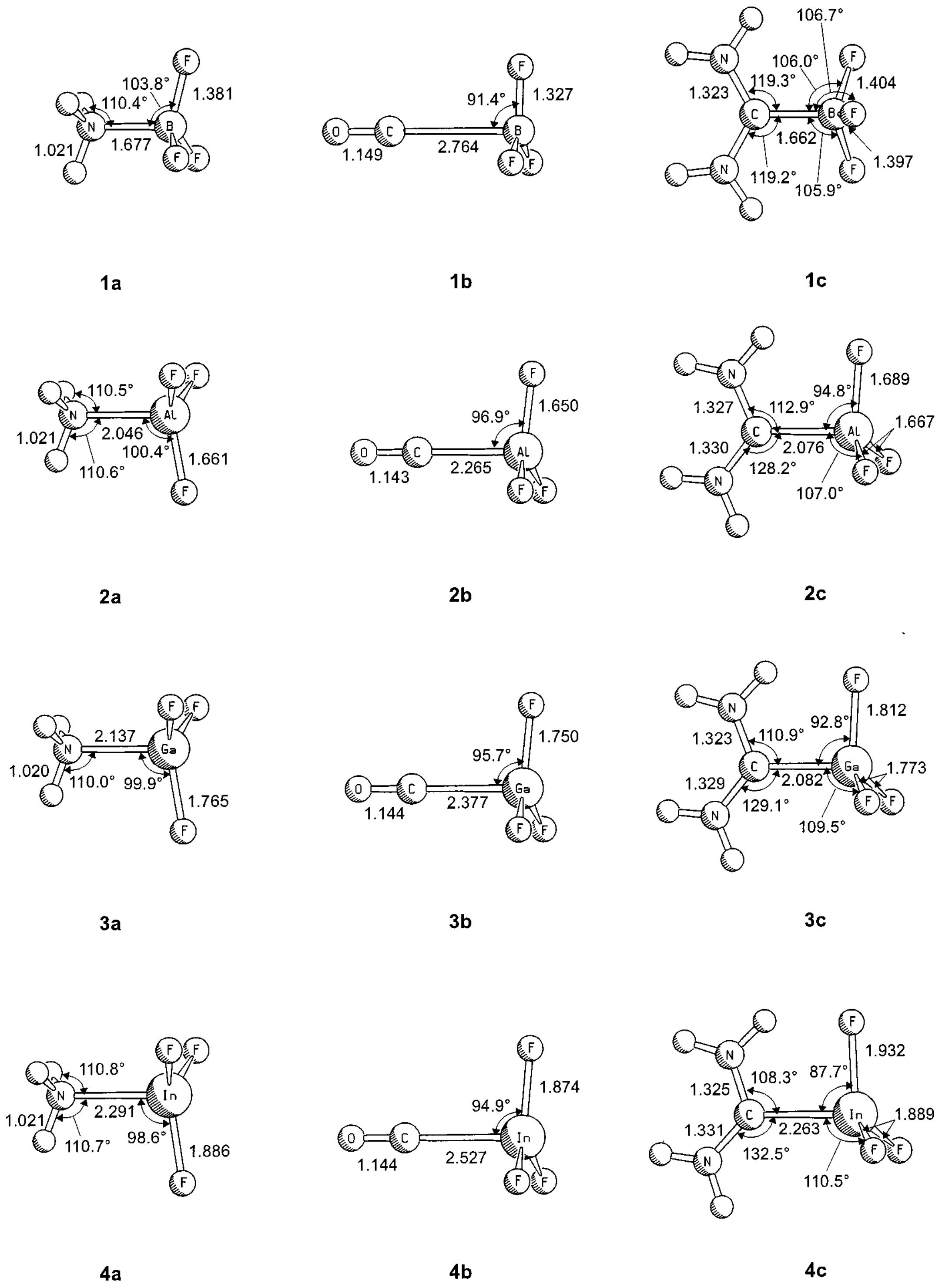
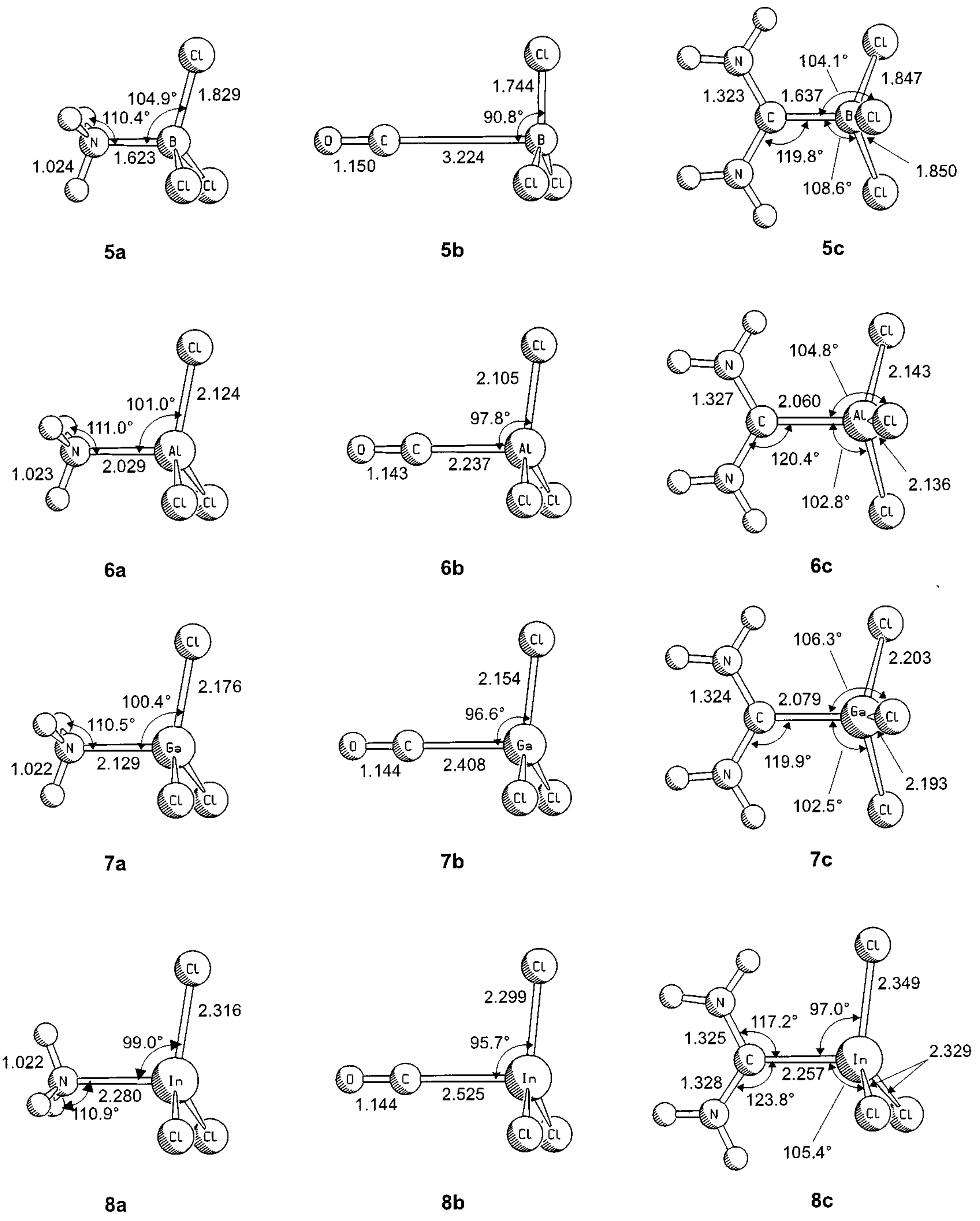


Figure 1. Optimized geometries of the complexes and fragments at the MP2/II level; bond lengths in Å, angles in degrees

kcal/mol). For all the complexes, the calculations show a clear trend in the Lewis basicities CO < NH_3 < $C(NH_2)_2$. CO is always significantly less strongly bonded (by 17−30 kcal/mol) in the complexes than NH_3, while $C(NH_2)_2$ is more strongly bonded (by 14−27 kcal/mol) than NH_3. The most strongly bonded CO complex is predicted to be F_3Al-CO (**2b**) (D_e = 15.1 kcal/mol). Note that CO forms particularly weak bonds with boron halides (D_e = 3.2 kcal/mol in **1b**, 2.3 kcal/mol in **5b**).

The calculated trends in the bond strengths of the Lewis acid adducts depend both on the nature of the Lewis base D and on the halogen atom. For the F_3E-D species, it is found that the complexes with E = Al, Ga, In, and the same ligand D have similar bond dissociation energies,



5a **5b** **5c**

6a **6b** **6c**

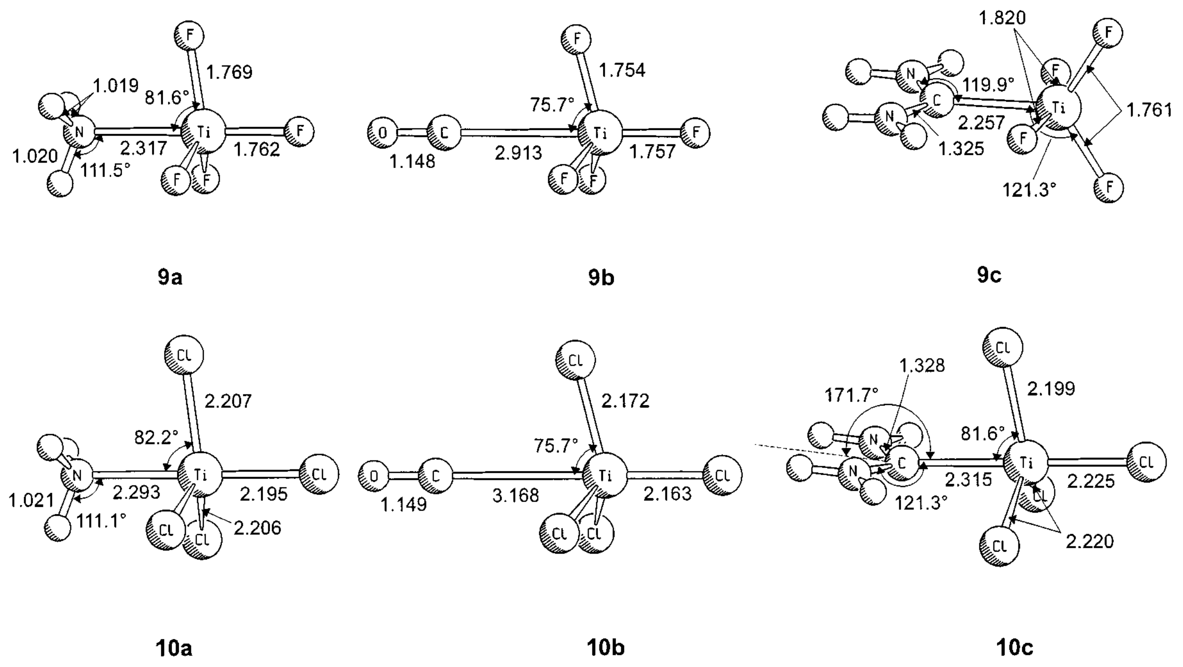
7a **7b** **7c**

8a **8b** **8c**

Figure 1. *(Continued)*

while the F_3B-D complexes are clearly less strongly bonded. The situation with the Cl_3E-D complexes is somewhat different. $Cl_3B-C(NH_2)_2$ (**5c**) has a higher bond dissociation energy (D_e = 59.7 kcal/mol) than the gallium complex **7c** (D_e = 57.5 kcal/mol) or the indium complex **8c** (D_e = 57.6 kcal/mol), and it is only slightly less strongly bonded than $Cl_3Al-C(NH_2)_2$ (**6c**) (D_e = 61.6 kcal/mol). NH_3, and particularly CO, form weaker bonds with BCl_3 than with the heavier analogues $AlCl_3$, $GaCl_3$, and $InCl_3$.

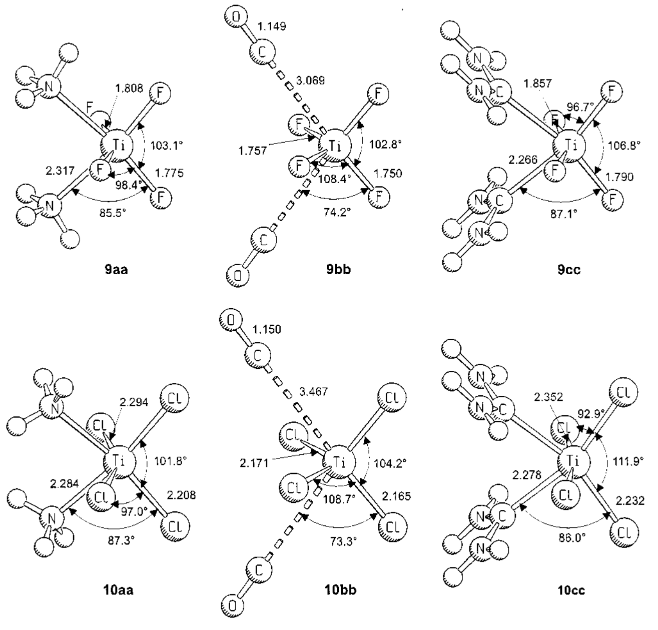
A comparison of the donor–acceptor bond strengths of the main group complexes with those of the transition metal compounds shows that for the three donor ligands D, TiF_4 and $TiCl_4$ have similar Lewis acidities as BF_3. The difference between the two groups of complexes is that TiF_4 and $TiCl_4$ can strongly bind *two* ligands D with almost the same bond strength, thereby yielding TiX_4D and TiX_4D_2, while main group Lewis acids show only weak affinities for binding more than one Lewis base.[2] Table 1 shows that in most cases the theoretical bond strengths of the first and second Ti–D bonds are similar. The second Ti–D bond may even be stronger than the first. For example, the energies required for dissociation of the first and second $C(NH_2)_2$ ligands from $Cl_4Ti[C(NH_2)_2]_2$ are 45.8 kcal/mol and 41.2 kcal/mol, respectively. The first and second am-



9a **9b** **9c**

10a **10b** **10c**

Figure 1. *(Continued)*



9aa **9bb** **9cc**

10aa **10bb** **10cc**

Figure 1. *(Continued)*

monia ligands of $Cl_4Ti(NH_3)_2$ are bound with similar bond strengths (D_e = 24.3 and 23.8 kcal/mol, Table 1). This is in contrast to the relative bond strengths in $OsO_4(NH_3)_2$, where the second NH_3 is clearly more weakly bound (D_e = 7.0 kcal/mol) than the first (D_e = 13.9 kcal/mol).[23b]

The theoretically predicted strong bonding of the first and second carbene ligands in $Cl_4Ti[C(NH_2)_2]_2$ is consistent with the experimental observation that the reaction of $MCl_4(THF)_2$ (M = Ti, Zr, Hf) with 1,3-dialkyl derivatives of imidazol-2-ylidene **A** may yield the respective monocarbene complex Cl_4TiD[32] or the dicarbene complex Cl_4TiD_2,[33] depending on the stoichiometry of the starting materials.

Experimental values for the bond energies are not available, but previous work on other donor−acceptor complexes carried out at the same level of theory showed that the theoretical values deviated by less than 3 kcal/mol from the experimental data.[23b] We believe the present values to have a similar degree of accuracy.

The geometries shown in Figure 1 reveal interesting aspects of the donor−acceptor interactions. We begin the discussion with the main group complexes **1a**−**8c**. It has previously been found that the B−F bond length in BF_3 becomes longer in donor−acceptor complexes $F_3B{-}D$, and that this extension of the B−F distance increases with increasing strength of the $F_3B{-}D$ bond.[23b] The data in Figure 1 and Table 1 show that this also holds true for the BF_3 complexes investigated here, i.e. the B−F bond length increases in the order BF_3 < **1b** < **1a** < **1c**. The same trend is calculated for the other E−F and E−Cl bond lengths. The carbonyl complexes invariably have the shortest E−X bonds, while the longest are found for the diaminocarbene complexes. A correlation of the $X_3E{-}D$ bond energies with the pyramidalization of the EX_3 moiety of **1a**−**8c** is also found. The angle D−E−X becomes larger in the order D = CO < NH_3 < $C(NH_2)_2$. Some D−E−X bond angles with D = $C(NH_2)_2$ become acute because of hydrogen bonding between one X atom and a proton of the amino group. In particular, the $F_3E{-}C(NH_2)_2$ complexes show an increased asymmetry about the E−C bond in the order **1c** < **2c** < **3c** < **4c**. Note the significant lengthening of the in-plane E−F

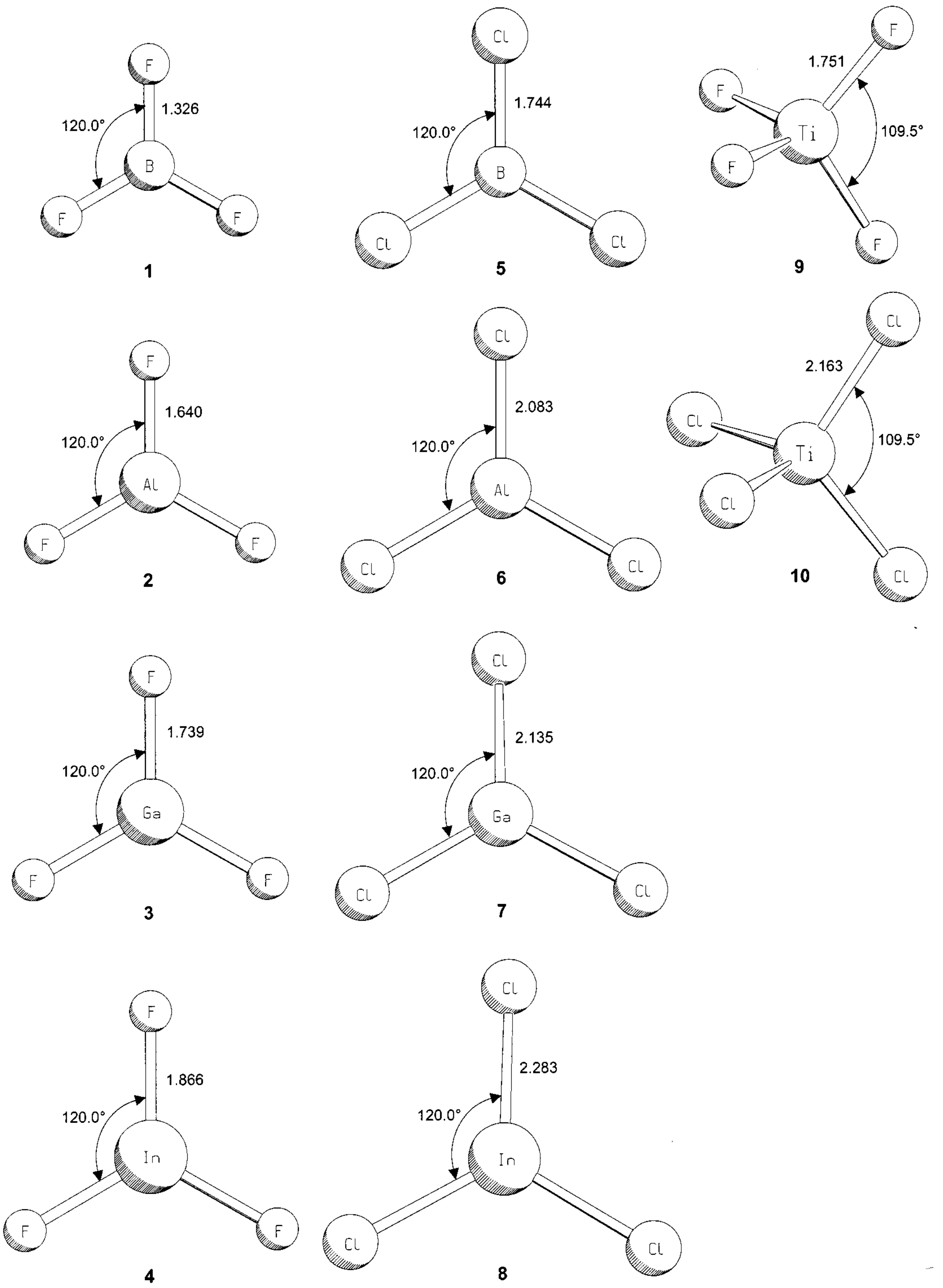


Figure 1. *(Continued)*

bond and the tilt of one amino group towards the in-plane fluorine atom in the complexes. Among the chlorine analogues, the same effect is found only for the indium complex **8c** (Figure 1).

The donor moieties in the pentacoordinated transition metal complexes X_4TiD have the ligand D *trans* to X, except in **9c**, where hydrogen bonding between fluorine and the amino group protons enforces an equatorial position of the carbene ligand. The diaminocarbene ligand in **10c** is slightly tilted from the N_2CTi plane (Figure 1). The hexacoordinated complexes X_4TiD_2 have the ligands D *cis* to one another. The *trans* forms (not shown here) are clearly higher in energy. This is in agreement with experimental evidence.[34]

We did not systematically calculate the activation barriers for rotation about the D−E bonds. However, some test cal-

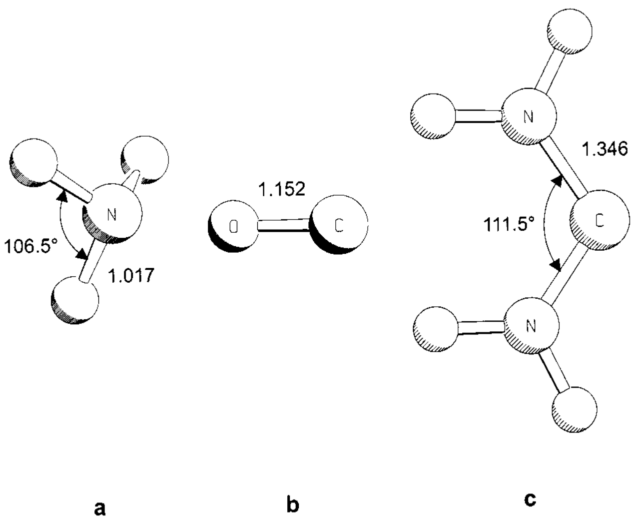


Figure 1. *(Continued)*

Table 1. Calculated total energies E_{tot} [Hartree] and zero-point vibrational energies ZPE [kcal/mol] at MP2/II+//MP2/II; theoretically predicted binding energies D_e [kcal/mol] and ZPE corrected values D_0 [kcal/mol]

Molecule	No.	Sym.	E_{tot}	ZPE	D_e	D_0
F_3B-NH_3	**1a**	C_{3V}	–380.51466	33.6	23.5	19.9
F_3B-CO	**1b**	C_{3V}	–437.15892	11.6	3.2	2.5
$F_3B-C(NH_2)_2$	**1c**	C_1	–473.73154	47.3	42.5	39.8
F_3Al-NH_3	**2a**	C_{3V}	–597.80920	30.2	43.4	40.4
F_3Al-CO	**2b**	C_{3V}	–654.44088	9.5	15.1	13.7
$F_3Al-C(NH_2)_2$	**2c**	C_S	–691.01919	44.3	58.0	55.5
F_3Ga-NH_3	**3a**	C_{3V}	–357.72434	29.0	38.5	35.6
F_3Ga-CO	**3b**	C_{3V}	–414.35976	8.2	12.5	11.3
$F_3Ga-C(NH_2)_2$	**3c**	C_1	–450.94453	43.4	59.5	56.8
F_3In-NH_3	**4a**	C_{3V}	–357.56041	28.4	40.9	38.2
F_3In-CO	**4b**	C_{3V}	–414.19446	7.8	14.2	13.0
$F_3In-C(NH_2)_2$	**4c**	C_S	–450.77772	42.9	60.1	57.5
Cl_3B-NH_3	**5a**	C_{3V}	–1460.36428	31.3	32.0	27.8
Cl_3B-CO	**5b**	C_{3V}	–1516.99364	8.5	2.3	1.8
$Cl_3B-C(NH_2)_2$	**5c**	C_1	–1553.59516	44.7	59.7	56.7
Cl_3Al-NH_3	**6a**	C_{3V}	–1677.68893	28.3	44.1	41.0
Cl_3Al-CO	**6b**	C_{3V}	–1734.31799	7.5	14.2	12.8
$Cl_3Al-C(NH_2)_2$	**6c**	C_1	–1770.90338	42.3	61.6	59.1
Cl_3Ga-NH_3	**7a**	C_{3V}	–1437.66573	27.4	35.4	32.6
Cl_3Ga-CO	**7b**	C_{3V}	–1494.30137	6.6	9.7	8.6
$Cl_3Ga-C(NH_2)_2$	**7c**	C_1	–1530.88756	41.6	57.5	55.1
Cl_3In-NH_3	**8a**	C_{3V}	–1437.49855	27.0	38.7	36.0
Cl_3In-CO	**8b**	C_{3V}	–1494.13263	6.3	12.0	10.9
$Cl_3In-C(NH_2)_2$	**8c**	C_S	–1530.71538	41.1	57.6	55.4
F_4Ti-NH_3	**9a**	C_1	–513.41667	31.3	24.1	21.3
F_4Ti-CO	**9b**	C_{3V}	–570.06356	10.3	5.4	4.5
$F_4Ti-C(NH_2)_2$	**9c**	C_1	–606.62625	45.9	38.5	35.7
Cl_4Ti-NH_3	**10a**	C_1	–1953.25375	29.0	24.3	21.2
Cl_4Ti-CO	**10b**	C_{3V}	–2009.89740	7.5	3.6	2.9
$Cl_4Ti-C(NH_2)_2$	**10c**	C_1	–2046.46737	42.7	41.2	39.0
$H_3N-F_4Ti-NH_3$	**9aa**	C_1	–569.86748	–	21.6	–
$OC-F_4Ti-CO$	**9bb**	C_S	–683.17536	–	7.3	–
$(NH_2)_2C-F_4Ti-C(NH_2)_2$	**9cc**	C_1	–756.29779	–	39.4	–
$H_3N-Cl_4Ti-NH_3$	**10aa**	C_1	–2009.71145	–	23.8	–
$OC-Cl_4Ti-CO$	**10bb**	C_S	–2123.00973	–	6.5	–
$(NH_2)_2C-Cl_4Ti-C(NH_2)_2$	**10cc**	C_1	–2196.15495	–	45.8	–
BF_3	**1**	D_{3h}	–324.05660	7.9	–	–
AlF_3	**2**	D_{3h}	–541.31953	5.1	–	–
GaF_3	**3**	D_{3h}	–301.24252	4.0	–	–
InF_3	**4**	D_{3h}	–301.07466	3.6	–	–
BCl_3	**5**	D_{3h}	–1403.89274	5.0	–	–
$AlCl_3$	**6**	D_{3h}	–1621.19804	3.1	–	–
$GaCl_3$	**7**	C_S	–1381.18872	2.5	–	–
$InCl_3$	**8**	C_S	–1381.01631	2.2	–	–
TiF_4	**9**	T_d	–456.95767	6.4	–	–
$TiCl_4$	**10**	T_d	–1896.79448	3.8	–	–
NH_3	**a**	C_{3V}	–56.42054	22.1	–	–
CO	**b**	$C_{\infty V}$	–113.09725	3.0	–	–
$C(NH_2)_2$	**c**	C_{2V}	–149.60721	36.7	–	–

culations showed that the rotational barriers appear to be very low, e.g. < 2 kcal/mol.

Analysis of the Bonding Situation

Table 2 shows the results of NBO analyses of the complexes. The data reveal some unexpected features concerning the bonding situations in the molecules.

The calculated $D \rightarrow EX_3$ charge donations in complexes of the Group 13 elements E show a marked difference between the boron halides and the heavier analogues. The charge donation $OC \rightarrow BX_3$ is negligible, while the charge donations $H_3N \rightarrow BX_3$ and $(NH_2)_2C \rightarrow BX_3$ are rather large. The $OC \rightarrow EX_3$ charge donation is greater for the heavier elements E = Al, Ga, In, while the $H_3N \rightarrow EX_3$ and $(NH_2)_2C \rightarrow EX_3$ charge transfer is less than that in the boron complexes. In fact, $OC \rightarrow EX_3$ and $H_3N \rightarrow EX_3$ charge donations are rather similar for the heavier Group 13 elements (Table 2). The calculated charge transfers in the Group 13 complexes suggest that the covalent character of the $OC-EX_3$ bond becomes stronger on going from E = boron (where it is practically nil) to E = Al, Ga, In, while the covalency of the H_3N-EX_3 and $(NH_2)_2C-EX_3$ bonds decreases on going from E = boron to E = Al, Ga, In.[35] This surprising result is supported by the calculated bond orders, which are clearly higher for the $OC-EX_3$ bonds of the heavier Group 13 elements than for boron, while the opposite order is calculated for the H_3N-EX_3 and $(NH_2)_2C-EX_3$ bonds (Table 2). The same conclusion can be drawn from the trend in the polarities of the $D-EX_3$ bonds. The donor–acceptor bond orbital is invariably polarized towards the donor atom. The polarization is higher for the $OC-BX_3$ bond (which is a pure carbon lone pair orbital) than for the heavier $OC-EX_3$ analogues, while the polarizations of the H_3N-EX_3 and $(NH_2)_2C-EX_3$ bonds show the opposite trend. However, in all cases, the donor–acceptor bonds of $C(NH_2)_2$ retain the highest covalent character of the three Lewis bases. The calculated charge donation $\Delta q(D \rightarrow A)$, the polarization, and the bond order of the D–A bonds indicate that the covalent character increases in the order $X_3B-CO < X_3B-NH_3 < X_3B-C(NH_2)_2$, while for the other Group 13 Lewis acids the trend is $X_3E-CO \approx X_3E-NH_3 < X_3E-C(NH_2)_2$.

The Ti–D bonds in the transition metal complexes have less covalent character than those in the Group 13 complexes. The NBO method finds a Ti–D bond orbital only for diaminocarbene complexes, while the TiX_4 complexes with CO and NH_3 as donor ligands have lone-pair orbitals at their donor atoms. The Ti–D bonds are mainly held together by the charge attraction between the large positive charge at the titanium atom and the negative charge of the lone-pair electrons. The calculated partial atomic charges do not reveal the extent of the charge interaction, which is strongly influenced by the topography of the anisotropic charge distribution.

An important feature is highlighted by the calculated hybridization at the Ti end of the $X_4Ti-C(NH_2)_2$ bonds.

Table 2. Results of the NBO analysis at the MP2/II level[a]

Molecule	No.	$\Delta q(D \rightarrow A)$	$q_{D(x)}$	$q_{A(y)}$	$D(x)-A(y)$							BO
					%x	%s(x)	%p(x)	%d(x)	%s(y)	%p(y)	%d(y)	
F_3B-NH_3	**1a**	0.29	–1.03	+1.34	84.71	31.08	68.91	0.02	19.97	79.40	0.62	0.46
F_3B-CO	**1b**	0.03	+0.44	+1.47	100.00	76.44	23.54	0.02	–	–	–	0.05
$F_3B-C(NH_2)_2$	**1c**	0.44	+0.27	+1.20	74.85	39.22	60.76	0.03	25.22	74.38	0.40	0.65
F_3Al-NH_3	**2a**	0.13	–1.19	+1.99	93.80	23.01	76.99	0.00	19.11	79.92	0.97	0.22
F_3Al-CO	**2b**	0.13	+0.44	+1.97	92.83	64.30	35.70	0.01	13.49	84.87	1.65	0.24
$F_3Al-C(NH_2)_2$	**2c**	0.19	+0.06	+1.92	88.95	34.15	65.85	0.00	21.77	76.41	1.82	0.34
F_3Ga-NH_3	**3a**	0.15	–1.16	+1.87	93.10	20.24	79.76	0.00	18.50	81.18	0.31	0.24
F_3Ga-CO	**3b**	0.12	+0.45	+1.86	93.45	63.44	36.55	0.01	12.16	87.12	0.72	0.22
$F_3Ga-C(NH_2)_2$	**3c**	0.23	+0.08	+1.79	86.78	33.25	66.75	0.00	23.39	75.57	1.04	0.40
F_3In-NH_3	**4a**	0.12	–1.18	+1.98	94.24	20.13	79.87	0.00	17.70	81.97	0.33	0.20
F_3In-CO	**4b**	0.10	+0.43	+1.97	94.50	63.12	36.86	0.01	12.26	87.72	0.02	0.19
$F_3In-C(NH_2)_2$	**4c**	0.19	+0.06	+1.91	88.58	32.32	67.67	0.00	22.77	77.16	0.08	0.35
Cl_3B-NH_3	**5a**	0.38	–1.01	+0.23	80.17	35.41	64.57	0.03	20.79	78.84	0.37	0.56
Cl_3B-CO	**5b**	0.01	+0.43	+0.29	100.00	76.91	23.06	0.02	–	–	–	0.02
$Cl_3B-C(NH_2)_2$	**5c**	0.50	+0.28	+0.11	69.63	40.94	59.02	0.04	25.50	74.30	0.20	0.73
Cl_3Al-NH_3	**6a**	0.16	–1.18	+1.47	92.20	28.81	71.18	0.00	19.30	79.59	1.10	0.26
Cl_3Al-CO	**6b**	0.18	+0.48	+1.35	89.08	65.87	34.13	0.00	13.68	84.70	1.62	0.34
$Cl_3Al-C(NH_2)_2$	**6c**	0.26	+0.08	+1.39	85.87	36.85	63.15	0.00	22.12	76.50	1.38	0.53
Cl_3Ga-NH_3	**7a**	0.18	–1.15	+1.38	91.54	26.30	73.70	0.00	18.04	81.73	0.23	0.27
Cl_3Ga-CO	**7b**	0.17	+0.49	+1.29	90.55	65.51	34.48	0.00	10.82	88.60	0.59	0.29
$Cl_3Ga-C(NH_2)_2$	**7c**	0.30	+0.12	+1.30	84.14	35.98	64.02	0.00	23.08	76.40	0.52	0.45
Cl_3In-NH_3	**8a**	0.16	–1.16	+1.60	92.42	24.20	75.80	0.00	17.13	82.79	0.08	0.25
Cl_3In-CO	**8b**	0.15	+0.47	+1.53	91.81	64.37	35.62	0.01	11.34	88.52	0.14	0.26
$Cl_3In-C(NH_2)_2$	**8c**	0.28	+0.12	+1.50	85.37	34.43	65.57	0.00	21.93	78.00	0.06	0.42
F_4Ti-NH_3	**9a**	0.12	–1.14	+2.02	100.0	39.66	60.34	0.00	–	–	–	0.20
F_4Ti-CO	**9b**	0.05	+0.44	+2.06	100.0	73.22	26.77	0.01	–	–	–	0.02
$F_4Ti-C(NH_2)_2$	**9c**	0.25	+0.11	+1.95	86.20	35.28	64.72	0.01	19.42	0.35	80.23	0.42
Cl_4Ti-NH_3	**10a**	0.20	–1.10	+0.61	100.0	40.86	59.14	0.00	–	–	–	0.26
Cl_4Ti-CO	**10b**	0.05	+0.44	+0.62	100.0	74.15	25.84	0.01	–	–	–	0.08
$Cl_4Ti-C(NH_2)_2$	**10c**	0.31	+0.20	+0.58	81.05	37.01	62.99	0.00	35.48	0.61	63.91	0.39
$H_3N-F_4Ti-NH_3$	**9aa**	0.14	–1.12	+1.89	100.0	36.33	63.66	0.01	–	–	–	0.22
$OC-F_4Ti-CO$	**9bb**	0.04	+0.44	+2.02	100.0	76.25	23.73	0.02	–	–	–	0.08
$(NH_2)_2C-F_4Ti-C(NH_2)_2$	**9cc**	0.23	+0.17	+1.74	100.0	36.29	63.70	0.01	–	–	–	0.39
$H_3N-Cl_4Ti-NH_3$	**10aa**	0.21	–1.08	+0.52	100.0	36.59	63.41	0.00	–	–	–	0.28
$OC-Cl_4Ti-CO$	**10bb**	0.02	+0.43	+0.63	100.0	76.93	23.05	0.02	–	–	–	0.04
$(NH_2)_2C-Cl_4Ti-C(NH_2)_2$	**10cc**	0.33	+0.24	+0.46	79.25	36.98	63.02	0.00	23.47	6.41	70.12	0.44

[a] Donor→acceptor charge donation Δq(D→A); partial atomic charges q of the donor atoms D(x) and acceptor atoms A(y); polarization of the donor−acceptor bond D(x)−A(y) in%x, hybridization of the D(x)−A(y) bond, Wiberg bond orders BO of the D(x)−A(y) bond.

Table 2 shows that the contribution from the 3d orbitals to the titanium−carbon bond is much greater than the 4s contribution. It has been suggested that the covalent bonds of the 3d elements are mainly formed by the 4s orbital and that the 3d orbitals are negligible.[36] However, the results presented here and elsewhere[37] show that this bonding model is not in agreement with quantum chemical calculations.

Finally, we would like to mention the NBO results concerning the bonding situation in the free diaminocarbene ligand. The calculations show that the formally vacant p(π) AO of the carbon atom in free $C(NH_2)_2$ is significantly populated by 0.67 e through N→C π-donation. This shows the importance of the allyl-anion-type delocalization in determining the stability of the diamino-substituted carbenes. The same conclusion was drawn from earlier theoretical studies.[38]

Summary and Conclusion

The calculations clearly show that diaminocarbene is a much stronger Lewis base than amines. This has been proven for donor−acceptor interactions with Group 13 trihalides and titanium tetrahalides, and probably holds true for complexes with other Lewis acids as well. The complexation energies of $C(NH_2)_2$ have been calculated to be 14−27 kcal/mol higher than those of NH_3. The most strongly bonded complex is $Cl_3Al-C(NH_2)_2$, which has a theoretically predicted Al−C bond energy D_o = 59.1 kcal/mol. BX_3 is clearly the weakest Lewis acid among the Group 13 trihalides. TiF_4 and $TiCl_4$ have similar Lewis acidities as BF_3, but the titanium tetrahalides may bind one or two donor molecules with almost the same bond strength. The donor−acceptor bonds have a high degree of ionic character. The greatest covalent contributions are found for the diaminocarbene complexes. The covalent character of the X_3E-CO bond becomes higher on going from E = boron to the heavier elements, while the opposite order is found for the X_3E-NH_3 and $X_3E-C(NH_2)_2$ bonds.

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