Angewandte
Correspondence

Chemical Bonding

DOI: 10.1002/anie.201311022

Dative Bonds in Main-Group Compounds: A Case for More Arrows!**

*Gernot Frenking**

bond theory · dative bonds ·
energy decomposition analysis ·
p-block coordination compounds

In their recently published essay, Himmel, Krossing, and Schnepf (HKS)[1] criticized the use of arrows in structural formulas for molecules of main-group elements which has become very popular in the last years. The increased occurrence of dative bonds for the description of main-group compounds in terms of donor–acceptor complexes can be traced back to our work ont the carbodiphosphorane $C(PPh_3)_2$ in 2006, where we suggested that based on its electronic structure and chemical behavior, the molecule is best described as a complex of a carbon atom in the excited ${}^1D$ state and two phosphane ligands $Ph_3P\rightarrow C\leftarrow PPh_3$.[2] This led to the introduction of carbones[3] CL_2 as compounds of divalent C^0 with two lone pairs of electrons at carbon. Carbones can be clearly distinguished by their electronic structure[4] and by their chemical reactivity[5] from carbenes CR_2, which are divalent C^{II} compounds. Examples for a continuous transition between the two bonding modes have been described by us.[6] Systematic theoretical studies showed that the bonding model of carbones CL_2 can be extended to the isoelectronic systems $(N^+)L_2$ and $(BH)L_2$[7] and to the heavy tetrylones EL_2 ($E = Si$–Pb).[8] The theoretical studies served as guideline for the syntheses of the borylene complex $(BH)L_2$[9] and the silylones SiL_2[10] as well as the germylones GeL_2[11] with different N-heterocyclic carbenes as ligands L.

Herein, I will take up the contraposition to the criticism of HKS and will show that the description of a previously unrecognized class of main-group compounds as donor–acceptor complexes is not only in agreement with experimental observations and with quantum chemical calculations; it has also proven to be a very useful model for classifying known compounds as well as for the prediction of new molecules with unusual bonds and reactivities. At the same time I want to reply to the criticism of HKS of the description of numerous molecules with the donor–acceptor bonding model. I also rebuke the allegation of the authors that the description of dative bonds is a marketing device, which should be considered "a deadly sin in academic behavior".[1] Finally, I want to show that HKS misunderstand the meaning of classical Lewis structures for describing bonding in molecules.

HKS write in their Essay: "In any case, dative bond arrows should be avoided, when one single conventional representation is entirely sufficient."[1] The authors suggest using classical Lewis structures as an alternative to dative bonds. They argue in all seriousness that classical formulas would have the advantage to be in agreement with "… all basic rules students learn (especially regarding the electronegativity differences)". Apparently, the basic rules taught in Freiburg and Tübingen are different from those I know from my courses and from textbooks. According to them, atomic charges which arise from mesomeric forms are purely formal numbers which may or may not agree with the actual charge distribution in a molecule. Thus, the formal charge of carbon in carbon monoxide which has the most important Lewis structure $|C\equiv O|$ is -1, while the partial charge at carbon is positive.[12] The formal charge of nitrogen in the most important Lewis structure for NH_4^+ possessing four N–H bonds is $+1$, but the partial charge of nitrogen is negative. The same holds true with opposite signs for BF_4^-, where boron in the most important Lewis structure carries a formal charge of -1 although its partial charge is strongly positive.[13] Writing ammonia borane $H_3N{-}BH_3$ as a zwitterion yields a negative charge at boron and a positive charge at nitrogen, while the partial charges exhibit the opposite polarity. Every student in a freshman chemistry course should know that Lewis structures do not provide direct information about the actual charge distribution in a molecule. It is a fundamental misunderstanding of HKS to take the formal description of the donor and acceptor moieties in a complex as an indication of the final charge distribution without considering the donor–acceptor interactions!

The criticism of HKS on the notation of dative bonds $A\rightarrow B$ is particularly incomprehensible, because the latter model does indeed provide information about the charge flow from the Lewis base to the Lewis acid and thus the charge distribution in the complex AB that arises from the bond formation. Accordingly, the presentation of the di- and trications $(P_4^{2+})(EPh_3)_2$ ($E = P$, As) and $(N^{3+})L_3$ ($L = cyclo$-$C_3(NMe_2)_2$) with formal charges at the acceptor units is by no means "nonsensical" or "nonsense" as stated by the authors but in agreement with theoretical and experimental results

---

[*] Prof. Dr. G. Frenking
Fachbereich Chemie, Philipps-Universität Marburg
Hans-Meerwein-Strasse, 35032 Marburg (Deutschland)
E-mail: frenking@chemie.uni-marburg.de

[**] I thank Prof. H. Grützmacher and Dr. R. Tonner for constructive comments and Markus Hermann for some of the graphics.

that consider the strength of the donor–acceptor interactions.[14] One of the great advantages of describing the molecules as complexes is that the the donor and acceptor strengths of A and B can give insight into the structure and stability of AB and homologues. This is shown in Figure 1 a for the isoelectronic complexes $E(PPh_3)_2$ with $E = BH, C, N^+$.

The calculated partial charge of −1.38[15] at the central atom of $(N^+)(PPh_3)_2$ is by no means an argument against the "counterproductive" description as a donor–acceptor complex, $Ph_3P{\rightarrow}N^+{\leftarrow}PPh_3$. Analogously, the partial charge of −1 for nitrogen in NH_4^+ does not speak against the (correctly understood) classical description with four N−H bonds and a formal N^+. The negative partial charges can be anticipated as result of the strong attraction of N^+ toward $(PPh_3)_2$ in $(N^+)(PPh_3)_2$ and toward $(H)_4$ in NH_4^+. The charge donation of 2.38 e in $(N^+)(PPh_3)_2$ means that the formation of each $P{\rightarrow}N^+$ bond is associated with a transfer of 1.19 e which indicates, as expected, a polarization towards the nitrogen atom. The charge donation of 1.43 e for $C(PPh_3)_2$ is of course smaller, because neutral ^1D-C is a weaker Lewis acid than ^1D-N^+. It is nevertheless quite large and therefore, the isoelectronic species BH in the excited reference state $^1\Delta$ in $(BH)(PPh_3)_2$ was also considered (Figure 1 a), where the lone pair of electrons occupies the p(π) atomic orbital of boron. The calculations gave a negative partial charge of −0.97 e at BH and surprisingly short and strong P−B bonds.[7]

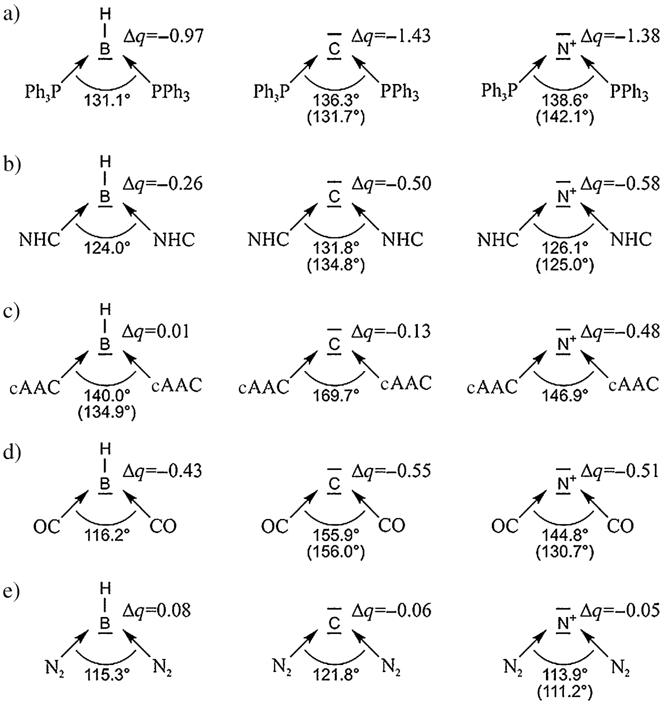


Figure 1. Calculated bond angles of isoelectronic molecules EL_2 and partial charges Δq of the central fragments $E = BH, C, N^+$.[7] Experimental values are given in parentheses.

However, the electronic reference state $^1\Delta$ of BH is 131.5 kcal mol^{-1} higher in energy than the $X^1\Sigma_g^+$ ground state. Therefore, even stronger binding ligands for $(BH)L_2$ have been explored. The first of these ligands were N-heterocyclic carbenes (NHCs) which might bind not only by means of NHC→(BH)←NHC σ donation but also through NHC←(BH)→NHC π backdonation. This was confirmed by quantum chemical calculations which suggested significantly stronger donor–acceptor bonds in $(BH)(NHC)_2$ than in $(BH)(PPh_3)_2$ (Figure 1 b).[7] This finally led to the successful isolation of the complex $(BH)(cAAC)_2$ (Figure 1 c), where the NHC ligands are replaced by cyclic alkyl amino carbenes (cAACs).[9] cAACs have only one nitrogen atom attached to the carbene carbon atom which further enhances the π backdonation cAAC←(BH)→cAAC. The description of the bonding situation in $(BH)(cAAC)_2$ with arrows, cAAC→(BH)←cAAC, immediately suggests a lone pair of electrons at boron, which agrees with the calculated electronic structure and with the reactivity of the borylene dicarbene. Again, it would be interesting to learn how HKS would write this in terms of Lewis structures. The same situation is given by the recently synthesized[16] coordination compound NHC→B≡B←NHC containing a boron–boron triple bond which was inspired by a theoretical study about dative bonds in main-group-element compounds E_2L_2 of Group 13 (E = B–In).[17]

The syntheses of $(BH)(cAAC)_2$[9] and the carbodicarbene $C(NHC)_2$,[18] which were suggested by our theoretical studies,[17,19] are clear evidence for the usefulness of the donor–acceptor model for predicting molecules that can be reasonably described with dative bonds.[20] Contrary to a posteriori depictions of experimental results in terms of Lewis structures, the model makes it possible to understand and to predict experimental findings. This becomes apparent when the bond angles L-E-L in the complexes EL_2 in Figure 1 are considered, which are easily understood with the help of the Dewar–Chatt–Duncanson (DCD) model.[21] The angle L-C-L is always larger than the angle L-(N^+)-L and the trend for the bond angles of the isoelectronic species $(N^+)(N_2)_2 = 111.2° < (N^+)(CO)_2 = 130.7° < C(CO)_2 = 156.0°$ is in agreement with the increase of the π backdonation L←E→L. The bond strengths of the complexes EL_2 and their stabilities can be estimated when one considers the electronic reference states of E and L and their excitation energies which are required for bond formation. For a detailed discussion I refer to the original publications.[4,7]

Carbon suboxide $C(CO)_2$ deserves particular attention. HKS state: "The question of whether the minimum structure of carbon suboxide is linear or bent in the gas phase is still not fully clarified." This statement does not agree with current knowledge. A careful investigation of the experimental vibrational spectrum[22] of C_3O_2 indicated the OC-C-CO angle to be 156°, which is in excellent agreement with quantum chemical calculations at the CCSD(T)/cc-pVQZ level, which give a value of 155.9°.[23] Carbon suboxide has a very shallow bending potential and it is considered to be a quasi-linear species that thermally equilibrates quite rapidly.[24] This does not alter the experimental and theoretical result that the equilibrium structure of C_3O_2 has a bending angle of 156° which should be explained with a bonding model. HKS suggest in their Figure 3 two mesomeric formulas that possess a negative charge at the central carbon atom and a positive charge at oxygen. Directly below the authors request that those mesomeric forms should be preferred which are in agreement with electronegativity differences!

A simple explanation for the nonlinear equilibrium geometry of C_3O_2 comes from the donor–acceptor bonding model (Figure 2) which HKS consider to be "extreme". The stepwise replacement of the phosphane ligands of $C(PPh_3)_2$ with the stronger π acceptor CO results in a widening of the bonding angle L-C-L, as expected from the DCD model for the geometries of transition-metal complexes. The more strongly bent geometries of the isoelectronic species $N^+(CO)_2$[25a] (144.8°) and $N^+(N_2)_2$[25b] (113.9°) may be explained in a straightforward fashion by using the model of donor–acceptor bonding with the weaker π backdonation of N^+. The transfer of the "extreme" model to complexes of main-group atoms provides an easy explanation for the trend of the bending angle without requiring a prior knowledge of the atomic partial charges.

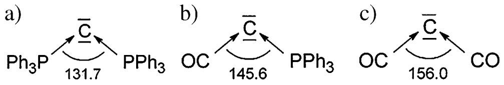


Figure 2. Experimental bond angles at the central carbon atom of the compounds $C(PPh_3)_2$, $C(PPh_3)(CO)$, and $C(CO)_2$.

Carbodiphosphorane $C(PPh_3)_2$ and carbodicarbene $C(NHC)_2$ are striking examples demonstrating the advantages of the description with dative bonds over that with a posteriori written mesomeric formulas. When the $C(PPh_3)_2$ was first synthesized in 1961 by Ramirez et al.[26] the authors assumed that the molecule has a linear structure which was described with the mesomeric formulae $Ph_3P{=}C{=}PH_3 \leftrightarrow Ph_3P^{(+)}{-}C^{(2-)}{-}{}^{(+)}PH_3$. Only in 1978 did an X-ay structure analysis show that $C(PPh_3)_2$ actually possesses a bent geometry with a bending angle of 131.7°.[27] This did not change the notation in terms of the mesomeric formulas for a long time,[28] until we showed in 2006[2] that the description in terms of dative bonds, $Ph_3P \rightarrow C \leftarrow PPh_3$, is a reasonable representation of the bonding situation in the molecule. This led to an understanding of the structures of numerous compounds EL_2 (examples are shown in Figure 1 and 2) and it became a guideline for the synthesis of new molecules with donor–acceptor bonds. The strongly bent geometry of $C(PPh_3)_2$ is easily rationalized when the molecule is considered to be a complex of a pseudo-quadruply coordinated carbon atom in the electronic ^1D state which exhibits two lone pairs of electrons and two PPh_3 ligands. Let us now turn to carbodicarbene $C(NHC)_2$. It is known from transition-metal chemistry that NHC and phosphanes PR_3 have similar donor properties.[29] In the light of the donor–acceptor model, the bent structure of $C(NHC)_2$ and the fact that the bending angle[18a,19] is similar to that in $C(PPh_3)_2$ is not surprising. A classical description which considers the octet rule and electronegativity differences would suggest a linear allene structure, $(NHC){=}C{=}(NHC)$.[30]

Not convinced yet? Then I want to discuss an example from recent research where the advantage of donor–acceptor bonding A→B and the distinction from electron-sharing bonding[31] A–B clearly come to the fore. In 2009, Roesky and co-workers isolated the compound $NHC \rightarrow SiCl_2$, which is definitely a donor-stabilized $SiCl_2$ (Figure 3 a).[32] The complex was reacted with the above-mentioned cAAC in which a ligand-exchange reaction was expected with formation of the more strongly bonded $cAAC \rightarrow SiCl_2$. Quantum chemical calculations predicted that the C–Si bond in the latter complex (Figure 3 b) is slightly shorter ($r_e = 1.949$ Å) and stronger ($D_e = 42.5\ \text{kcal mol}^{-1}$) than that in $NHC \rightarrow SiCl_2$ (measured $r_e = 1.985$ Å, calculated bond dissociation energy $D_e = 40.5\ \text{kcal mol}^{-1}$). However, the reaction gave the completely different product $SiCl_2(cAAC)_2$ where two cAAC ligands are bonded to Si with significantly shorter Si–C bonds ($r_e = 1.845$ Å, exp.; 1.849 Å, calc.; Figure 3 c) than those in the calculated complex $cAAC \rightarrow SiCl_2$.[33] But $SiCl_2$ has only *one* vacant coordination site! The experimental finding can be explained by a changeover from a dative bond in $NHC \rightarrow SiCl_2$ to electron-sharing bonds in $cAAC{-}Si(Cl_2){-}cAAC$.

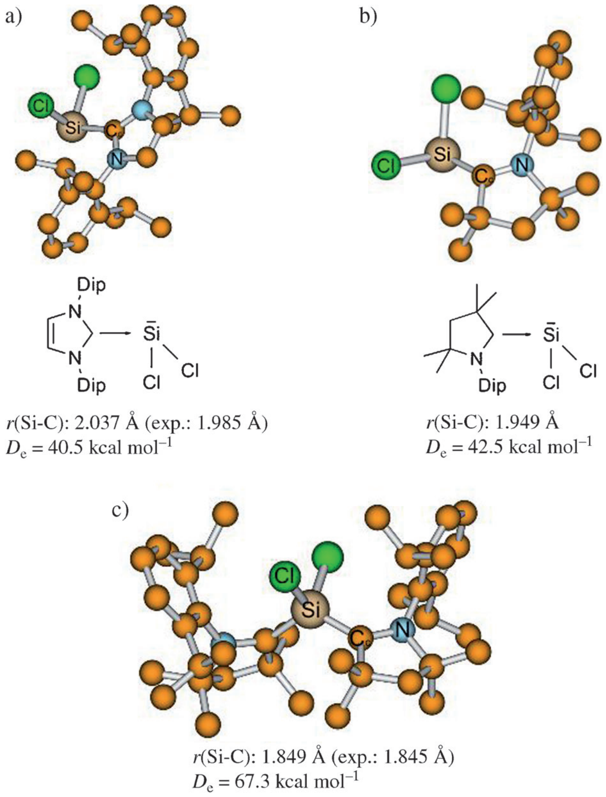
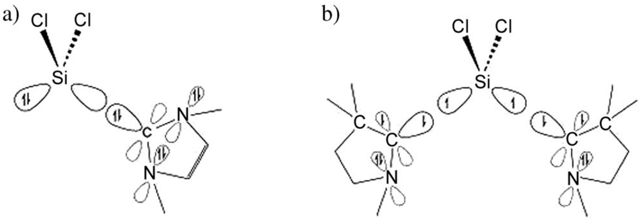


Figure 3. Equilibrium geometries of a) $NHC \rightarrow SiCl_2$; b) $cAAC \rightarrow SiCl_2$; c) cAAC-Si(Cl$_2$)-cAAC. Calculated bond dissociation energies D_e of the ligands NHC and cAAC.[33]

A change from the singlet to the triplet state of $SiCl_2$ and the cAAC ligands affords the formation of two Si–C electron-sharing bonds. But it means that the two unpaired electrons that remain at the cAAC ligands occupy two spatially separated orbitals. According to Hund's second rule, this should lead to a triplet state which is indeed the case: The EPR spectrum of $Si(Cl_2)(cAAC)_2$ showed the signal for a triplet state.[33] Electron-sharing bonds are usually shorter and stronger than donor–acceptor bonds between the same atoms, which agrees with the calculated Si–C distances in $cAAC \rightarrow SiCl_2$ and $cAAC{-}Si(Cl_2){-}cAAC$. For the comparison of the bond strengths it is necessary to consider the electronic excitation energy of the $SiCl_2$ and cAAC fragments from the singlet ground state to the triplet reference state. Figure 4 shows that the calculated value for breaking the Si−C electron-sharing bonds of $Si(Cl_2)(cAAC)_2$ yielding triplet fragments amounts to $D_e = 227.5$ kcal mol^{-1}. Subtracting the singlet–triplet excitation energies of $SiCl_2$ and cAAC gives a net stabilization of 67.3 kcal mol^{-1} which is larger than the bond dissociation energy of cAAC→$SiCl_2$ ($D_e = 42.5$ kcal mol^{-1}). In contrast, $SiCl_2(NHC)_2$ with Si−C electron-sharing bonds is not formed, because the singlet–triplet excitation energy of NHC is much higher (88.9 kcal mol^{-1}) than that of cAAC (49.9 kcal mol^{-1}).



ΔE(S/T; NHC^{Dip}) = 88.9 kcal mol^{-1}

ΔE(S/T; $SiCl_2$) = 60.1 kcal mol^{-1}
ΔE(S/T; cAAC^{Dip}) = 49.9 kcal mol^{-1}
D_e(T) = 227.2 kcal mol^{-1}

Figure 4. Schematic representation of the bonding situation in a) NHC→$SiCl_2$; b) cAAC−Si(Cl_2)−cAAC. Calculated singlet–triplet excitation energies ΔE(S/T) of the fragments.[33]

Similarly it can be explained why $C(CO)_2$ exhibits dative bonds, OC→C←CO, and a bent geometry while CO_2 possesses electron-sharing bonds and a linear structure, O=C=O.[34] Electron-sharing bonds, OC=C=CO, would require that the CO ligands are excited from the singlet to the triplet state, which costs 139.1 kcal mol^{-1} for each ligand.[35] In contrast, no electronic excitation energy is necessary for the electron-sharing bonds in CO_2, because the oxygen atoms have a ^3P triplet ground state. This pattern of explanation goes back to the work of Carter and Goddard[36a] and Trinquier and Malrieu[36b] which found widespread application in main-group chemistry, particularly for understanding the differences between the molecular structures of first-octal-row elements and higher homologues.[37]

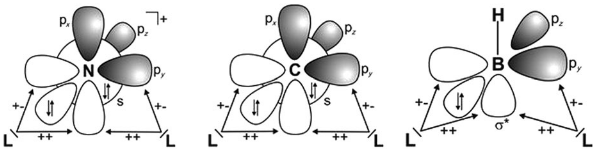
The difference between dative bonds and electron-sharing bonds and its relevance was discussed in a review article by Haaland in 1989.[38] HKS cite this work as evidence against the use of dative bonds in carbones CL_2 and in cations like $(N^+)L_2$ as well as dications $(P_4^{2+})(EPh_3)_2$ (E = P, As). Haaland suggested that dative bonds are characterized by their weakness and their rather long interatomic distances and by a small degree of charge transfer. According to HKS, all three criteria are not fulfilled in the above molecules. But Haaland defined his criteria for dative bonds on the basis of donor–acceptor complexes that were known in 1989, which are largely restricted to classical Group 13/15 adducts. The usefulness of the donor–acceptor model for describing carbodiphosphorane $C(PPh_3)_2$, the consequential perception of carbones CL_2 as divalent carbon(0) compounds, the extension to valence isoelectronic molecules EL_2 with E = N^+, BH, Si–Pb and to complexes with other numbers of ligands EL_n where $n = 1$, 3, and finally the large area of coordination compounds with multidentate acceptor fragments such as E_2L_2 (E = Si–Pb; B–In; N–Bi) and $(P_4^+)L_2$ has been suggested, discussed, and applied only in work that was published after our first paper about dative bonds in carbodiphosphorane[2] had appeared in 2006.[39] The work after 2006 is not a contradiction to but an extension of the knowledge about dative bonds as they were discussed by Haaland. Dative bonds can be very strong and short and they may be associated with a significant charge transfer. Dative bonds A−B can be distinguished from electron-sharing bonds by their heteropolar dissociation A−B→A + |B while the latter are characterized by homopolar bond breaking A−B→A• + B•.[52]

In the context of using the model of dative bonds for dications, I want to draw the attention of the readers to a work from 1986 where we calculated the unusual structures of species with the general formula CH_2X^{2+} and CH_4X^{2+} with X = HF, H_2O, NH_3, N_2, F_2, H_2, CO, CH_2, and CH_4 which had been studied in the gas phase.[40] It turned out that the equilibrium geometries of the dications were frequently quite different from those of the neutral parent systems. Rather exotic structures were found which did not correspond to classical forms, but they could be described with dative bonds that explained their stabilities. Likewise, the very unusual minimum-energy geometries on the E_2H_2 (E = Si–Pb) potential energy surface, which are difficult to describe with Lewis structures, can easily be explained in terms of donor–acceptor interactions.[41] HKS should note: *Bonding models are not right or wrong but they are more or less useful.*[42]

An aspect that was completely ignored by HKS is the quantitative support of the donor–acceptor bonding model by modern methods of bonding analysis which were employed in the criticized work. The description of carbones CL_2 and homologues EL_2 with dative bonds, L→E←L, was not based solely on plausible arguments. We did not content ourselves with a simple inspection of the shape and energy of the orbitals, which clearly showed that the highest occupied orbitals of $C(PPh_3)_2$ consist of two orbitals with π symmetry (HOMO) and σ symmetry (HOMO−1).[2] The electronic structure of the molecules was investigated with an energy decomposition analysis (EDA)[43] which makes it possible to estimate the strength of the σ donation L→E←L and π backdonation L←E→L as well as all other components of the interatomic interactions.[4,7] The results of the EDA and EDA-NOCV calculations[44] (NOCV = natural orbitals for chemical valence) provide comprehensive insight into the nature of the chemical bond.[45] For a description of the methods[43,44] and for exemplary applications[46] I refer to the original work. Here I want to introduce the EDA-NOCV results of the complexes $(N^+)L_2$, CL_2 and $(BH)L_2$ where L = PPh_3, NHC which demonstrate the potential of a bonding analysis using modern methods of quantum chemistry.[7]

At the top of Table 1 the most important orbital interactions are shown schematically which can be expected from a qualitative view of the electronic structures of the donors L and the acceptors E (N^+, C, BH) in the electronic singlet reference state. There is σ donation L→E←L from the in-

Table 1: EDA-NOCV calculations of the donor–acceptor complexes $(N^+)L_2$, CL_2, and $(BH)L_2$ with L = PPh_3, NHC. Energy values in kcal mol^{-1}.



Acceptor	N^+		C		BH	
Ligand	$(PPh_3)_2$	$(NHC)_2$	$(PPh_3)_2$	$(NHC)_2$	$(PPh_3)_2$	$(NHC)_2$
ΔE_{int}	−447.1	−509.6	−192.3	−267.3	−223.6	−314.4
ΔE_{Pauli}	724.8	881.1	738.4	917.6	229.7	279.0
ΔE_{elstat}[a]	−219.3	−350.8	−284.0	−354.6	−154.8	−224.0
	(18.7 %)	(25.2 %)	(30.5 %)	(29.9 %)	(34.1 %)	(37.8 %)
ΔE_{orb}[a]	−952.6	−1039.9	−646.7	−830.4	−298.6	−369.3
	(81.3 %)	(74.8 %)	(69.5 %)	(70.1 %)	(65.9 %)	(62.2 %)
$\Delta E_{\sigma 1}$ L→E←L	**−503.6**	**−598.4**	**−384.2**	**−517.7**	**−123.9**	**−140.5**
(+,+) donation[b]	**(52.9 %)**	**(57.5 %)**	**(59.4 %)**	**(62.3 %)**	**(41.5 %)**	**(38.0 %)**
$\Delta E_{\sigma 2}$ L→E←L	**−392.6**	**−361.2**	**−190.5**	**−196.0**	**−90.4**	**−102.4**
(+,−) donation[b]	**(41.2 %)**	**(34.7 %)**	**(29.5 %)**	**(23.6 %)**	**(30.3 %)**	**(27.7 %)**
ΔE_{π} L←E→L	**−23.9**	**−39.1**	**−65.0**	**−98.8**	**−78.0**	**−108.2**
π-backdonation[b]	**(2.5 %)**	**(3.8 %)**	**(10.1 %)**	**(11.9 %)**	**(26.1 %)**	**(29.3 %)**
ΔE_{rest}[b]	−32.5	−41.2	−6.9	−17.8	−6.3	−18.2
	(3.4 %)	(4.0 %)	(1.1 %)	(2.1 %)	(2.1 %)	(5.0 %)
ΔE_{prep}	83.6	116.5	63.6	87.3	139.0	166.6
D_e	363.5	393.1	128.6	180.0	84.6	147.8

[a] The values in parentheses give the percentage contribution to the total attractive interactions $\Delta E_{elstat} + \Delta E_{orb}$. [b] The values in parentheses give the percentage contribution to the total orbital interactions ΔE_{orb}.

phase (+,+) component of the electron lone-pairs of L_2 into the vacant $2p_x$ AO of N^+ or C in the ^1D state and the vacant sp hybrid orbital of BH ($^1\Delta$), respectively. The out-of-phase (+,−) σ donation[47] of L_2 takes place into the $2p_y$ AO of E. The π backdonation L←E→L comes from the occupied $2p_{z^2}$ AO of E into vacant π orbitals of L_2.

The intrinsic interaction energies ΔE_{int} between donor and acceptor that are calculated by the EDA-NOCV method suggest that NHC is a significantly stronger Lewis base than PPh_3 and that the strength of the donor–acceptor bonds in EL_2 follows the trend for E: $N^+ > BH > C$ (Table 1).[48,49] The data further show that the covalent contributions (ΔE_{orb}) to the bonds are clearly larger than the electrostatic attraction (ΔE_{elstat}). The calculated values for the three pairwise contributions $\Delta E_{\sigma 1}$, $\Delta E_{\sigma 2}$, and ΔE_{π} to the orbital interactions may be used to estimate the strength of the donor–acceptor interactions which are schematically shown at the top of Table 1. The strongest contributions to ΔE_{orb} come from the (+,+) and (+,−) components of the σ donation L→E←L with the trend $(N^+) > C > (BH)$, which can be expected on the basis of their electronegativities. The results show furthermore that NHC is always a better σ donor[50] but also a stronger π acceptor than PPh_3. The strength of the L←E→L π backdonation exhibits the expected trend $(N^+) < C < (BH)$. Note that the π backdonation in $(BH)L_2$ has a comparable strength to that of the components of the σ donation. It follows that BH in the $^1\Delta$ state in the calculated complexes[51] is an equally good σ acceptor and π donor, while N^+ and C in the ^1D state are largely σ acceptors. The EDA-NOCV method provides a detailed and quantitative picture of the nature of the chemical bond in the molecules EL_2, which can be connected to the qualitative model of orbital interactions.

Of course, one may ignore all the new insights and prospects available from applications of the donor–acceptor bonding model to main-group compounds that extend beyond the limits of earlier ideas.[38] The wealth of experimental results in recent years on compounds with unusual bonds which have been described using arrows[39] is actually clear evidence for its usefulness. The transfer of the DCD model from transition-metal chemistry, where this concept is successfully employed and accepted as a heuristic paradigm disregarding the difference between formal charges and real charge distribution, has been a sustainable enrichment for the area of main-group compounds. It is certainly possible to describe in hindsight the molecules with mesomeric formulas. But then one should at least know the difference between formal charges of Lewis structures and the real charge distribution in a molecule. However, it takes a hefty dose of impudence to insinuate that those authors, who describe main-group compounds with dative bonds, do so as a “marketing gimmick”! After reading the essay of HKS I got the impression that the bonding lines of Lewis structures have mutated into bars in front of their eyes that prevent them from recognizing new findings.

Received: December 19, 2013

---

[1] D. Himmel, I. Krossing, A. Schnepf, *Angew. Chem.* **2014**, *126*, 378; *Angew. Chem. Int. Ed.* **2014**, *53*, 370.

[2] R. Tonner, F. Öxler, B. Neumüller, W. Petz, G. Frenking, *Angew. Chem.* **2006**, *118*, 8206; *Angew. Chem. Int. Ed.* **2006**, *45*, 8038.

[3] R. Tonner, G. Frenking, *Pure Appl. Chem.* **2009**, *81*, 597.

[4] a) R. Tonner, G. Frenking, *Chem. Eur. J.* **2008**, *14*, 3260; b) R. Tonner, G. Frenking, *Chem. Eur. J.* **2008**, *14*, 3273.

[5] B. Inés, M. Patil, J. Carreras, R. Goddard, W. Thiel, M. Alcarazo, *Angew. Chem.* **2011**, *123*, 8550; *Angew. Chem. Int. Ed.* **2011**, *50*, 8400.

[6] a) S. Klein, R. Tonner, G. Frenking, *Chem. Eur. J.* **2010**, *16*, 10160; b) C. Esterhuysen, G. Frenking, *Chem. Eur. J.* **2011**, *17*, 9944; c) S. R. Barua, W. D. Allen, E. Kraka, P. Jerabek, R. Sure, G. Frenking, *Chem. Eur. J.* **2013**, *19*, 15941.

[7] M. A. Celik, R. Sure, S. Klein, R. Kinjo, G. Bertrand, G. Frenking, *Chem. Eur. J.* **2012**, *18*, 5676.

[8] a) N. Takagi, T. Shimizu, G. Frenking, *Chem. Eur. J.* **2009**, *15*, 3448; b) N. Takagi, T. Shimizu, G. Frenking, *Chem. Eur. J.* **2009**, *15*, 8593; c) N. Takagi, G. Frenking, *Theor. Chem. Acc.* **2011**, *129*, 615.

[9] R. Kinjo, B. Donnadieu, M. A. Celik, G. Frenking, G. Bertrand, *Science* **2011**, *333*, 610.

[10] a) K. C. Mondal, H. W. Roesky, F. Klinke, M. C. Schwarzer, G. Frenking, B. Niepötter, H. Wolf, R. Herbst-Irmer, D. Stalke, *Angew. Chem.* **2013**, *125*, 3036; *Angew. Chem. Int. Ed.* **2013**, *52*, 2963; b) Y. Xiong, S. Yao, S. Inoue, J. D. Epping, M. Driess, *Angew. Chem.* **2013**, *125*, 7287; *Angew. Chem. Int. Ed.* **2013**, *52*, 7147.

[11] a) Y. Xiong, S. Yao, G. Tan, S. Inoue, M. Driess, *J. Am. Chem. Soc.* **2013**, *135*, 5004; b) Y. Li, K. C. MOndal, H. W. Roesky, H. Zhu, P. Stollberg, R. Herbst-Irmer, D. Stalke, D. M. Andrade, *J. Am. Chem. Soc.* **2013**, *135*, 12422.

[12] The unusual dipole moment of −0.12 D for CO, which has the negative pole at carbon, is sometimes taken as support for the Lewis structure $:C\equiv O:$. This is a false conclusion which comes from a misunderstanding of both Lewis structures and dipole moments. For a detailed discussion of the electronic structure and bonding situation in CO, see: G. Frenking, C. Loschen, A. Krapp, S. Fau, S. H. Strauss, *J. Comput. Chem.* **2007**, *28*, 117.

[13] The calculation of the partial charges with the NBO method gives in NH_4^+ $q(N) \approx -1$ while for BF_4^- $q(B) \approx +1$ is found. The values are quite independent from the level of theory. It would be interesting to learn which mesomeric forms are suggested by HKS for these and other molecules discussed herein that agree with their electronegativities and/or equilibrium geometries.

[14] At the end of their Essay,[1] the authors voiced their concern that future work might even sketch molecules with F^+ as an acceptor. They will be shocked to learn that a molecule has been synthesized and calculated which can reasonably be described with the formal bonding situation $D \rightarrow F^+$. W. Petz, B. Neumüller, D. Andrade, G. Frenking, manuscript in preparation.

[15] HKS give a value of −1.55 in their Essay[1] while citing our work.[7] The reason for the discrepancy is unknown to us. Table 4 in our work gives $q(N^+) = -1.38$. The difference between the two values is irrelevant for the discussion.

[16] H. Braunschweig, R. D. Dewhurst, K. Hammond, J. Mies, K. Radacki, A. Vargas, *Science* **2012**, *336*, 1420; see also the commentary: G. Frenking, N. Holzmann, *Science* **2012**, *336*, 1394.

[17] N. Holzmann, A. Stasch, C. Jones, G. Frenking, *Chem. Eur. J.* **2011**, *17*, 13517.

[18] a) C. A. Dyker, V. Lavallo, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2008**, *120*, 3250; *Angew. Chem. Int. Ed.* **2008**, *47*, 3206; b) A. Fürstner, M. Alcarazo, R. Goddard, C. W. Lehmann, *Angew. Chem.* **2008**, *120*, 3254; *Angew. Chem. Int. Ed.* **2008**, *47*, 3210.

[19] R. Tonner, G. Frenking, *Angew. Chem.* **2007**, *119*, 8850; *Angew. Chem. Int. Ed.* **2007**, *46*, 8695.

[20] An example of the improper use of the donor–acceptor model is found in the paper by Schmidbaur and Schier, where the authors discuss spiro compounds of carbon as donor–acceptor complexes with π-bonded ligands: H. Schmidbaur, A. Schier, *Angew. Chem.* **2013**, *125*, 187; *Angew. Chem. Int. Ed.* **2013**, *52*, 176.

[21] a) M. J. S. Dewar, *Bull. Soc. Chim. Fr.* **1951**, *18*, C79; b) J. Chatt, L. A. Duncanson, *J. Chem. Soc.* **1953**, 2929; c) G. Frenking, *J. Organomet. Chem.* **2001**, *635*, 9; d) G. Frenking, *Modern Coordination Chemistry: The Legacy of Joseph Chatt* (Eds.: G. J. Leigh, N. Winterton), The Royal Society, London, **2002**, p. 111.

[22] P. Jensen, J. W. C. Johns, *J. Mol. Spectrosc.* **1986**, *118*, 248.

[23] J. Koput, *Chem. Phys. Lett.* **2000**, *320*, 237.

[24] J. Van der Auwera, J. W. C. Johns, O. L. Polansky, *J. Chem. Phys.* **1991**, *95*, 229.

[25] a) I. Bernhardi, T. Drews, K. Seppelt, *Angew. Chem.* **1999**, *111*, 2370; *Angew. Chem. Int. Ed.* **1999**, *38*, 2232; b) K. O. Christe, W. W. Wilson, J. A. Sheehy, J. A. Boatz, *Angew. Chem.* **1999**, *111*, 2112; *Angew. Chem. Int. Ed.* **1999**, *38*, 2004.

[26] F. Ramirez, N. B. Desai, B. Hansen, N. McKelvie, *J. Am. Chem. Soc.* **1961**, *83*, 3539.

[27] G. E. Hardy, J. I. Zink, W. C. Kaska, J. C. Baldwin, *J. Am. Chem. Soc.* **1978**, *100*, 8002.

[28] O. I. Kolodiazhnyi, *Tetrahedron* **1996**, *52*, 1855.

[29] W. A. Herrmann, *Angew. Chem.* **2002**, *114*, 1342; *Angew. Chem. Int. Ed.* **2002**, *41*, 1290.

[30] Tetraaminoallenes $(R_2N)_2C{=}C{=}C(NR_2)_2$ with acyclic diaminocarbene units $C(NR_2)_2$ possess a linear or nearly linear geometry which depends on the size of the groups R.[19] The reactivity of tetraaminoallenes resembles that of carbones CL_2 and therefore, they have been termed "hidden carbones".[4b] For experimental work see: H. G. Viehe, Z. Janousek, R. Gompper, D. Lach, *Angew. Chem.* **1973**, *85*, 581; *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 566.

[31] There are no standardized terms for distinguishing between a dative bond $A \rightarrow B$, which is also called a donor–acceptor or coordinative bond, and an electron-sharing bond A–B, which is sometimes called a "normal" covalent bond. Haaland uses the terms dative bond and covalent bond for the different types which is misleading. Both donor–acceptor bonds $A \rightarrow B$ and electron-sharing bonds A−B arise from covalent interactions due to the interference of the wave functions of A and B.

[32] R. S. Ghadwal, H. W. Roesky, S. Merkel, J. Henn, D. Stalke, *Angew. Chem.* **2009**, *121*, 5793; *Angew. Chem. Int. Ed.* **2009**, *48*, 5683.

[33] K. C. Mondal, H. W. Roesky, M. C. Schwarzer, G. Frenking, S. Neudeck, I. Tkach, H. Wolf, D. Kratzert, R. Herbst-Irmer, B. Niepötter, D. Stalke, *Angew. Chem.* **2013**, *125*, 1845; *Angew. Chem. Int. Ed.* **2013**, *52*, 1801.

[34] Stronger π-acceptor ligands than L = CO may lead to a linear structure L-C-L. Dative bonds can be recognized in such cases by a very shallow bending potental and by chemical reactivity that is typical for carbones CL_2. An example are the tetraaminoallenes mentioned in Ref. [30].[4b,19]

[35] K. P. Huber, G. Herzberg, *Constants of Diatomic Molecules*, Van Nostrand-Reinhold, New York, **1979**.

[36] a) E. A. Carter, W. A. Goddard, *J. Phys. Chem.* **1986**, *90*, 998; b) G. Trinquier, J.-P. Malrieu, *J. Am. Chem. Soc.* **1987**, *109*, 5303.

[37] a) M. Driess, H. Grützmacher, *Angew. Chem.* **1996**, *108*, 900; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 828; b) M. Lein, A. Krapp, G. Frenking, *J. Am. Chem. Soc.* **2005**, *127*, 6290.

[38] A. Haaland, *Angew. Chem.* **1989**, *101*, 1017; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 992.

[39] I refer to the long list of publications which are cited as reference [1] in the paper by HKS.[1] For the most recent publication on this topic see A. M. Tondreau, Z. Benkö, J. Harmer, H. Grützmacher, *Chem. Sci.* **2014**, *5*, 1545.

[40] W. Koch, G. Frenking, J. Gauss, D. Cremer, *J. Am. Chem. Soc.* **1986**, *108*, 5808.

[41] See Ref. [37b].

[42] H. Primas, U. Müller-Herold, *Elementare Quantenchemie*, 2nd ed., Teubner, Stuttgart, **1990**, p. 289.

[43] T. Ziegler, A. Rauk, *Theor. Chim. Acta* **1977**, *46*, 1.

[44] M. P. Mitoraj, A. Michalak, T. Ziegler, *J. Chem. Theory Comput.* **2009**, *5*, 962.

[45] The difference between the EDA and EDA-NOCV methods lies in the ability of the NOCV approach to separate the orbital interactions ΔE_{orb} into pairwise contributions of the fragments. The EDA permits only the separation of ΔE_{orb} into contributions arising from orbitals that belong to one irreducible representation of the molecular point group.

[46] Reviews: a) M. von Hopffgarten, G. Frenking, *WIREs Comput. Mol. Sci.* **2012**, *2*, 43; b) M. Lein, G. Frenking in *Theory and Applications of Computational Chemistry: The First 40 Years* (Eds.: C. E. Dykstra, G. Frenking, K. S. Kim, G. E. Scuseria), Elsevier, Amsterdam, **2005**, p. 367; c) G. Frenking, K. Wichmann, N. Fröhlich, C. Loschen, M. Lein, J. Frunzke, V. M. Rayón, *Coord. Chem. Rev.* **2003**, *238–239*, 55; d) M. Lein, A. Szabó, A. Kovács, G. Frenking, *Faraday Discuss.* **2003**, *124*, 365; G. te Velde, F. M. Bickelhaupt, E. J. Baerends, S. J. A. van Gisbergen, C. Fonseca Guerra, J. G. Snijders, T. Ziegler, *J. Comput. Chem.* **2001**, *22*, 931.

[47] The symmetry assignments for σ and π donation are made with respect to the *xy* plane.

[48] The stronger interaction ΔE_{int} of BH in the $^1\Delta$ state compared with ^{1}D-C comes from the significantly weaker Pauli repulsion $\Delta E_{\mathrm{Pauli}}$ in $(\mathrm{BH})\mathrm{L}_2$ in comparison with CL_2. The attractive terms ΔE_{orb} and $\Delta E_{\mathrm{elstat}}$ are weaker in $(\mathrm{BH})\mathrm{L}_2$ than in CL_2. The bond dissociation energy D_{e} gives after relaxation of the fragments into the electronic ground state the trend $\mathrm{N}^+ > \mathrm{C} > \mathrm{BH}$.

[49] A stronger bond does not necessarily mean that the attractive terms are stronger than in a weaker bond. It can also come from weaker Pauli repulsion. An example are CO and N_2. The attractive components of the bonding in CO are weaker than in N_2 but the Pauli repulsion in carbon monoxide is clearly weaker than in dinitrogen: C. Esterhuysen, G. Frenking, *Theor. Chem. Acc.* **2004**, *111*, 381. Erratum: C. Esterhuysen, G. Frenking, *Theor. Chem. Acc.* **2005**, *113*, 294.

[50] The $(+,-)$ component of the σ donation $\mathrm{L}\rightarrow(\mathrm{N}+)\leftarrow\mathrm{L}$ for PPh_3 is stronger than for NHC, which is likely due to the better overlap in the phosphane complex. For the sum of the $(+,+)$ and $(+,-)$ σ donation holds that NHC is a stronger donor than PPh_3.

[51] The donor and acceptor strength of the central fragment E in EL_2 depends of course on the electronic properties of the ligands L. Thus, the central carbon atom C in $\mathrm{C(CO)}_2$ is also a π donor, because CO is a relatively strong π acceptor.

[52] Dative bonds of polar compounds $[\mathrm{A}\rightarrow\mathrm{B}]^q$ may encounter crossing of potential energy curves which can lead to homopolar bond breaking.