Bonding Models

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

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coordinative bonds · covalent bonds · dative bonds · p-block coordination compounds

In recent years bond arrows "→" have been used more and more frequently in the structural formulae of main-group compounds.[1,2] Thereby, the terminology of a central atom and ligand as introduced by Alfred Werner 100 years ago is transferred from transition-metal chemistry to the main-group elements. For example, the neutral compound L_2Si_2 [L = N-heterocyclic carbene] was discussed as a Si^0 compound[3] and described as a new "soluble allotrope" of silicon in a simultaneously published Perspectives article in *Science* (Figure 1).[4]

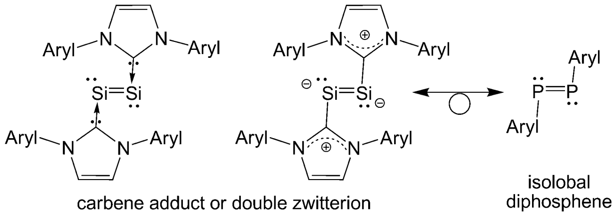

Figure 1. Mesomeric formulae for neutral L_2Si_2 [L = N-heterocyclic carbene] and its relation to the isolobal diphosphenes.

Following this nomenclature the influence of the carbene ligand should be rather small, which is doubtful considering the calculated Si–C bond energy of 169 kJ mol^{-1}. Similarly $[Fe_2(CO)_9]$ and $[Fe_3(CO)_{12}]$, for example, could equally well be declared as soluble allotropes of iron. Nevertheless, the description of L_2Si_2 using dative bonds still seems to be appropriate, although the formulation as double zwitterion, which emphasizes the relation to the isolobal diphosphenes (Figure 1), would certainly have a similar weight and would have been helpful for the straightforward understanding of its electronic structure.

However, the excessive use of the concept "main-group-element coordination compounds" can lead to counterproductive descriptions, which may contradict both experimental and theoretical findings. In this Essay we will illustrate this notion based on three compound types selected from a large variety of current examples (Figure 2): The long-known PPN cation ($=[N(PPh_3)_2]^+$) was reinterpreted as a $Ph_3P\rightarrow N^+\leftarrow PPh_3$ coordination compound.[5] The $[P_4(AsPh_3)_2]^{2+}$ ion,[6] obtained in a very unusual reaction, was denoted as a donor–acceptor adduct of the $[P_4]^{2+}$ dication with Ph_3As, thus as $Ph_3As\rightarrow P_4^{2+}\leftarrow AsPh_3$. The final example we discuss is $[N(\leftarrow L)_3]^{3+}$ (L = cyclo-$C_3(NMe_2)_2$),[7] which was promoted in the title of the publication as a "carbene-stabilized N-centered cation," in which a N^{3+} cation is supposed to adopt the role of an acceptor. In our opinion these selling descriptions, especially when used as the sole representation, should be rejected, as we will discuss here.

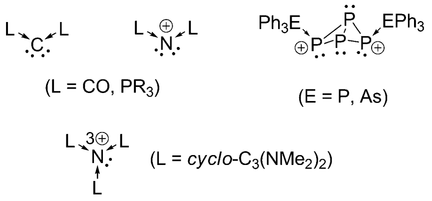

Figure 2. Notation of the structures discussed in the text with dative bonds.

Bonding descriptions in such molecules/ions are based on upon concepts to aid in understanding the structural, physical, and chemical properties. Since concepts often simplify, it is important to consider their limits and to apply them carefully. With respect to the nature of the chemical bond there are always splendid debates, since it is itself a concept and often no corresponding physical observable can be measured. As a result, the question of which notation should be taught in student courses and written in current textbooks has to be clarified in discourse. The description of main-group molecules/ions by a single, electron-precise Lewis formula is often very limiting. Nevertheless, for most compounds an extended description with several mesomeric formulae, and which is in agreement with the experimental structure and the determined physical/chemical properties, can be found.

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In a very readable article in this journal,[8] Haaland noted characteristic features of a dative bond represented by an arrow "→" are that it is weak,[9] longer than a typical single bond, and has a rather small degree of charge transfer. Starting from the prototypical compounds ethane and ammine–borane, the properties of which are listed in Table 1, Haaland recommended differentiating between normal and dative bonds. Normal bonds include covalent and ionic bonds as well as bonds of medium polarity. According to his definition, homolytic bond cleavage is preferred for normal bonds in the gas phase and heterolytic cleavage for dative bonds.

Table 1: Properties of ethane, methylammonium, and ammine–borane.

Property	$H_3C{-}CH_3$	$[H_3C{-}NH_3]^{+[a]}$	$H_3B{\leftarrow}NH_3$
$\Delta_{diss}H°$ [kJ mol^{-1}]	377[b]	466[b]; 439[c]	130[c]
d [pm]	153	151	166
μ [D]	0	2.2	5.2

[a] Calculated with the G3 method. [b] Homolysis. [c] Heterolysis.

Daniel Himmel studied chemistry at the Universität Karlsruhe (TH) and completed his PhD thesis in the group of Prof. M. Scheer in 2004. In the same year, he joined the group of Prof. I. Krossing at the Ecole Polytechnic Federale de Lausanne (EPFL). He was a DFG fellow from 2005 to 2007 and moved with the Krossing group to Freiburg in 2006. His current interests focus on quantum chemical calculations on acidities and redox potentials as well as on the further development of preparative synthetic techniques.

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Haaland's analysis clearly demonstrates that there are smooth transitions between the different kinds of bonds. An example is the isoelectronic methyl ammonium cation $[H_3C{-}NH_3]^+$, which is isoelectronic to the prototypes listed in Table 1. The energies of its homolytic and heterolytic bond cleavage, 466 and 439 kJ mol^{-1}, respectively, are rather similar, but according to Haaland's criterion, the dative bonding description $[H_3C{\leftarrow}NH_3]^+$ is favored. However, the assignment of the methyl ammonium ion as an ammonia-complexed methyl cation is in contradiction to its reactions. This shows that a single rigid criterion for evaluating model descriptions is an obstructive oversimplification. Therefore, we argue for a pragmatic assessment of bonding descriptions using dative arrows and/or partial charges: Both descriptions should be used within reasonable limits and in agreement with the determined and calculated properties of the compound. An example of a very well-balanced description can be found in a recently published article by Schmidbaur and Schier.[10] In any case, dative bond arrows should be avoided, when one single conventional representation is entirely sufficient. In the following we will demonstrate this transition.

From bold to nonsensical: Compounds of the type $[R_2P{-}PR'_3]^+$ are described as a phosphonium as well as a ligand-stabilized phosphenium ion $[R_2P{\leftarrow}PR'_3]^+$.[11–15] The Lewis acid R_2P^+, the basis for the dative bond description, is well defined and a known stable compound with substituents like $N(i\text{Pr})_2$.[16] As such, the description is certainly bold but makes sense, and in the cited articles a balanced description with dative bond arrows and also as onium ions is used.

Carbones: More difficult to evaluate are the interesting theoretical analogies between well-known compounds like C_3O_2 and carbodiphosphoranes.[17,18] In this context, the new class of carbon(0) complexes $(L{\rightarrow})_2C$, the so-called carbones, was postulated; for a critical commentary, see Reference [19]. The question of whether the minimum structure of carbon suboxide is linear or bent in the gas phase is still not fully clarified.[20–22] For both, C_3O_2 and hexaphenylcarbodiphosphorane, the calculated highly negative partial charge of the central C atom (−0.55 and −1.43, respectively)[18] is in better agreement with the classical Lewis formula and the octet rule. The long-standing dispute on the contributions of possible hypervalent bonding will not be discussed here; these can also be discussed without invoking a dative bond (Figure 3 bottom in brackets).[23]

The PPN cation as a coordination compound? We had followed the discovery of the carbones with interest and, despite some skepticism, we took this unusual perspective seriously and as a valid contribution to the discussion. More recently the long-known PPN cation[24,25] was presented as

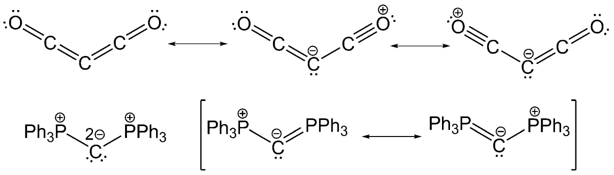

Figure 3. Classical mesomeric formulae of carbon suboxide and hexaphenylcarbodiphosphorane.

a N^+ complex $Ph_3P{\rightarrow}N^+{\leftarrow}PPh_3$,[7] although the charge accumulated at the central atom, formulated as a N^+ cation, was calculated to amount to −1.55(!). In the redefined “phosphane-stabilized N^+ electrophile $[N(PPh_3)_2]^+$, the formal phosphane ligand is not even substituted by the strong nucleophile ”naked fluoride“. Quite in contrast, according to Knapp et al. fluoride adds to one of the P atoms instead.[26] Moreover, the P–N bonds are neither weak nor long. Thus, the zwitterionic formulation $Ph_3P^+{-}N^-{-}P^+Ph_3$, which follows all basic rules students learn (especially regarding the electronegativity differences), would have been much more logical here.

A ligand-stabilized $[P_4]^{2+}$ cation? To claim $[P_4(AsPh_3)_2]^{2+}$ as ligand-stabilized $[P_4]^{2+}$ seems to be inappropriate, particularly as the conventional Lewis notation (Figure 4 top) accounts for the typical single bond lengths found in the experiment and the calculated partial charges very well (according to the calculation in Reference [6] +0.12 on the P_4 unit and +1.88(!) on the two $AsPh_3$ units together). Using the dative bond description, the charge transfer between the $AsPh_3$ unit and the P_4 core would be 0.94. Even for the extreme case of ethane as an adduct of CH_3^- and CH_3^+, the charge transfer of 1.0 would be only minimally larger!

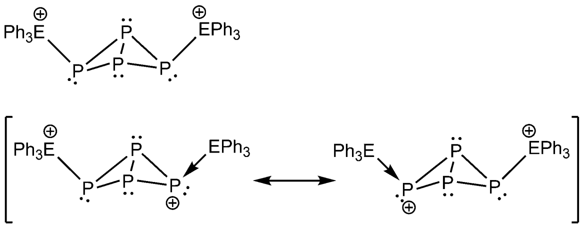

Figure 4. Mesomeric formulae of $[Ph_3E{-}P_4{-}EPh_3]^{2+}$ (E = P, As) considering the experimentally observed exchange of As^+Ph_3 for PPh_3 (see text).

None of the three characteristics of a dative bond mentioned by Haaland (weak bond, long distance, small charge transfer) are met. On the contrary, the average enthalpy of the heterolysis is 388 kJ mol^{-1} per As–P bond (cf. ammine–borane: 130 kJ mol^{-1}). In consideration of these facts, the description as a diarsonium ion $Ph_3As^+{-}P_4{-}As^+Ph_3$ would be more reasonable. Phosphenium ion character can—if at all—be discussed on the basis of a slight admixture of the form $Ph_3E^+{-}P_4^+{\leftarrow}EPh_3$ (Figure 4 bottom).[27] Thereby, the experimentally observed exchange of $AsPh_3$ for PPh_3 might be accounted for in this way.[28]

Ligand-stabilized N^{3+}? For the “ligand-stabilized N^{3+}”, as it is claimed in the title of the publication, two “extreme mesomeric formulae” are presented (Figure 5).[5] In our opinion, the rather conventional structure on the left-hand side of Figure 5 would nearly be sufficient to describe this cation as a reasonably good approximation, despite the many other possible resonance formulae. By contrast, the second structure, which serves as an argument for the publication title, has no basis in reality. Mesomeric formulae should not be evoked to be as “far away” from the bonding situation as possible but rather offer reasonable resonance structures with relevant weight. An NPA analysis delivers the charge of the central N atom as −0.45 and the authors themselves concluded that the conventional resonance structure of the compound is more in line with its properties than the description as a ligand-stabilized trication. Why wasn't this conclusion reflected in the title of the publication? We do not hesitate to consider the right-hand formula in Figure 5 nonsense.

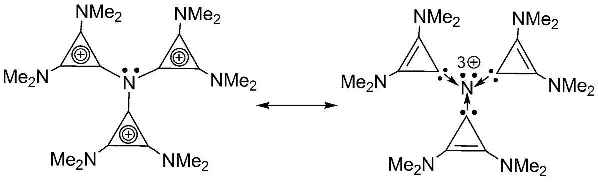

Figure 5. Extreme descriptions…?

New pseudo compound classes: Does the logic of the above examples even suggest the “discovery” of the “oxygenes” as ligand-stabilized oxygen(0) compounds (Figure 6)? Spectacular pseudo compound classes can easily be constructed along these lines. It needs to be clarified, though, whether the description yields new insight or only a “selling point”.[29]

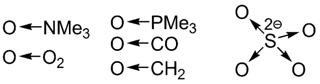

Figure 6. Examples for “oxygenes”, ligand-stabilized oxygen(0) compounds, as pseudo compound classes.

Extreme notation? In order to emphasize one aspect of a compound, it may well be discussed like this. However, it should not be marketed based on such an extreme notation with little weight.[29] We are happy to accept a new, unusual point of view as a contribution to the discussion—but it should be noted as such. In particular, we anticipate the risk that especially young scientists might be misled by a one-sided approach. Why not consider $[Ph_3E{-}P_4{-}EPh_3]^{2+}$ as a conventional diarsonium/diphosphonium dication, which totally agrees with all experimental data and calculations? Is there any intellectual profit in describing a negatively polarized nitrogen atom through the use of arrows as cationic N^{3+}? Not much imagination is needed to extrapolate what might come next: Will the long-known $[Ph_3P{-}O{-}PPh_3]^{2+}$ dication[30,31] be advertized as ligand-stabilized oxygen(2+) compound? Is the hitherto undisclosed oxidation state +1 for fluorine on the horizon (Figure 7)?

We appeal to all authors to identify extreme formulations as unusual notations and to elaborate on their value in the

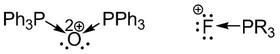

Figure 7. Phosphane-stabilized O^{2+} and F^+?

discussion. The introduction of single notations that are in strong contradiction to the results of experiments and calculations should be discouraged.

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[23] At this point it has to be considered that upon reinterpretation as "carbone" the oxidation state of the central carbon atoms is changed by 4 units compared to the traditionally taught form. The concept of oxidation states is certainly not the first choice to discuss the here elucidated bonding situation. Nevertheless, using the dative notation creates carelessly an additional ambiguity.

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from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[27] An admittedly rough estimate might be appropriate here: Even if all E–P bonds have 10% dative character in analogy to Figure 3, the bis-dative $[Ph_3E{\rightarrow}P_4{\leftarrow}EPh_3]^{2+}$ structure would contribute $0.1^2 = 1\,\%$ to the total bond situation.

[28] However, model calculations rather suggest an associative mechanism to form Ph_3P^+-P_4-P^+Ph_3 from Ph_3As^+-P_4-As^+Ph_3.

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