Silver Acetylene Complexes (1)

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Comments on “Homoleptical Silver(I) Acetylene Complexes”

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In a recent publication, Krossing, Scherer, and co-workers[1] report interesting experimental results about homoleptical Ag^I acetylene complexes. However, misleading statements are made when it comes to the interpretation of the X-ray analysis which is discussed below. Krossing, Scherer, and co-workers say that the stabilization of the $[Ag(\eta^2\text{-}C_2H_2)_n]^+$ ions ($n=1, 3, 4$) in the presence of the weakly coordinating anion (WCA) $[Al(OR^F)_4]^-$ takes place under “pseudo-gas phase conditions”. They further write that by using a WCA even weakly bound Lewis acid–base complexes can be formed “to complement gas-phase investigations with structural information and other physical properties that can only be obtained in condensed phases.”

The statements are misleading, because they suggest that the influence of a condensed phase on the structure of the investigated species may be neglected. But it has been well known for a long time that intermolecular interactions, even under so-called “inert” conditions of a noble-gas matrix, may have a strong impact on the structure and even on the existence of molecules. This holds particularly for polar and charged compounds. For example, the equilibrium distance of the donor–acceptor complex $HCN–BF_3$ in the gas phase is N–B (2.473 ± 0.029) Å while in the solid state it is N–B (1.638 ± 0.002) Å.[2] The shortening by approximately 0.8 Å in the solid state does not complement gas-phase investigations but it is rather a hint that single-crystal structure analysis by X-ray diffraction does not capture a single molecule but rather the result of the sum of interatomic *and* intermolecular interactions. The latter may have a strong impact on the structure but also on the bonding situation in a molecule. A recent first X-ray structure analysis of a free borole showed that the C–C and C–B distances exhibit surprisingly balanced values which suggest an unusual conjugation of the four π electrons in the antiaromatic five-membered ring. High-level quantum chemical calculations predict clearly alternating bond lengths which agree with the expected values for an antiaromat. More detailed investigations and model calculations of a dimer show that intermolecular interactions are responsible for the distortion of the geometry of free borole.[3]

There are further issues in the work of Krossing, Scherer, and co-workers[1] which need to be corrected. For example, the authors emphasize the good agreement between the calculated B3LYP values for the geometry of $[Ag(\eta^2\text{-}C_2H_2)][Al\{OC(CH_3)(CF_3)_2\}_4]$ (compound **3** in ref. [1]) and the results of the X-ray structure analysis which let them conclude: “This fine agreement supports the quality of the experimental study.” This fine agreement is not only rather an example for a fortuitous error cancellation between the neglect of intermolecular interactions and the chosen quantum chemical approximate method, it also intrinsically disproves the alleged “pseudo-gas phase conditions” in the solid state. A geometry optimization at the same level as chosen by Krossing, Scherer, and co-workers for the free cation $[Ag(\eta^2\text{-}C_2H_2)]^+$ gives an Ag–C bond which is 0.06 Å longer than it is calculated for **3**. This means that even the influence of the electric field of a single counterion induces a significant shortening of the Ag–C distance which clearly confutes the statement that the conditions of the free cations resemble those in the gas phase. The object of the X-ray structure analysis is neither free $[Ag(\eta^2\text{-}C_2H_2)]^+$ nor free **3** but $(\mathbf{3})_\infty$. It is very important to realize the relevance of intermolecular interactions, particularly for weakly binding interactions in the salts of the $[Ag(\eta^2\text{-}C_2H_2)_n]^+$ cations ($n=3, 4$) which have been synthesized by Krossing, Scherer, and co-workers. In an earlier theoretical study we could show that the shortening of a weak bond in a solid state may be estimated with an approximate exponential curve after calculating the bond strength of the free molecule.[4] The crucial role of the condensed phase for the structure of coordination complexes has been emphasized in two recent investigations which carefully analyze the differences between the geometries of molecules in the gas phase and in the solid state.[5]

We also criticize the statement from Krossing, Scherer, and co-workers about the nature of the Ag–C bonds in complex **3** which is based on a superficial interpretation of the topological analysis of the electron density. The bond paths of the $[Ag(\eta^2\text{-}C_2H_2)]^+$ cation exhibit a T-shaped structure which has no bond critical points for the Ag–C bonds. This is a strong argument in favor of a dominantly electrostatic interaction. Examples for T-shaped structures rather than cyclic structures have already been discussed.[6] However, the Laplacian $\nabla^2\rho(\mathbf{r})$ of **3** shows a polarization of the valence shell of the silver atom. Krossing, Scherer, and co-workers write: “Such a polarization scenario is in clear

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conflict with earlier theoretical studies that assumed an electrostatic bonding scenario for silver acetylene complexes.” The alleged conflict does not exist, because the polarization of the charge distribution at the Ag atom may equally be the result of purely inductive interactions with the anisotropical charge distribution of the acetylene ligand. It is conspicuous that Krossing, Scherer, and co-workers use only the numerical data of the $C{\equiv}C$ bond when they discuss the results of the topological analysis of **3** and 2,2′ethynylenedibenzoic acid (compound **4** in ref. [1]) while the values for the bond critical point of the bond path between Ag and the midpoint of the $C{\equiv}C$ bond which is termed TCP give a much more direct information about the silver–acetylene interactions. The topological data for the TCP are found in the Supporting Information. There is a positive value for the Laplacian at the TCP $\nabla^2\rho(\mathbf{r}) = 5.51\,e\,\mathrm{\AA}^{-5}$ which according to Bader[7] is a clear evidence for electrostatic interactions while the $C{\equiv}C$ bond has a strongly negative value $\nabla^2\rho(\mathbf{r}) = -29.58\,e\,\mathrm{\AA}^{-5}$ which signifies a covalent bond. An even stronger argument in favor of an electrostatic Ag–(C_2) interaction comes from the calculated energy density. It was shown as early as in 1984 by Cremer and Kraka that the energy density at the bond critical point $H(\mathbf{r}_b)$ is a very sensitive criterion for the nature of a chemical bond.[8] Covalent bonds have negative values $H(\mathbf{r}_b) < 0$, while ionic bonds and van der Waals bonds have $H(\mathbf{r}_b) \approx 0$. We carried out a topological analysis of **3** at BP86/TZVPP and we found for the TCP the value $H(\mathbf{r}_b) = -0.06$ Hartree $\mathrm{\AA}^{-3}$. For the $C{\equiv}C$ bond we calculate $H(\mathbf{r}_b) = -4.06$ Hartree $\mathrm{\AA}^{-3}$. This clearly shows that the silver–acetylene bond in **3** should be considered as electrostatic, which is in agreement with the T-shape of the bond paths, with the positive value for the Laplacian and with the results of previous theoretical studies.[9]

Further criticism concerns the calculated complexation energies which are given in Table 1 in ref. [1] for the homoleptic ions $[Ag(\eta^2\text{-}C_2H_2)_n]^+$ ($n = 1$–4). The complexation energy of a single acetylene ligand in the complex $[Ag(\eta^2\text{-}C_2H_2)_4]^+$ is calculated at MP2/TZVPP with a value of $-39.8\,\mathrm{kJ\,mol^{-1}}$ (MP2/QZVPP: $-35.3\,\mathrm{kJ\,mol^{-1}}$). However, Krossing, Scherer, and co-workers neglect entropic and thermal effects which are very important for the intrinsic stability of the free cations in the gas phase. After entropy correction the calculation of the free complexation energy at MP2/TZVPP for a temperature of −20 °C gives $\Delta G(253\,\mathrm{K}) = -11.9\,\mathrm{kJ\,mol^{-1}}$. This means that free $[Ag(\eta^2\text{-}C_2H_2)_4]^+$ hardly exists in the gas phase. The substantial stabilization in the solid state could be determined by measuring the heat of sublimation which would be an important contribution to the understanding of the intermolecular interactions, which are totally neglected by Krossing, Scherer, and co-workers.

Krossing, Scherer, and co-workers announce in their Communication that in a forthcoming full paper they will provide a “full account of all aspects” which arise from the comparison of previous gas-phase studies with their results of the X-ray structure analysis. They declare already that theoretical models which were used to explain the shorter $C{\equiv}C$ distances in the solid state compared with gas phase values “are immature”. We recommend a careful reading of recent studies which point out the crucial role of the condensed phase for the geometry of coordination complexes.[5] Krossing, Scherer, and co-workers are well advised to realize that the object of their solid-state investigations is a different species than a free molecule in the gas phase. This difference is not eliminated even when they use a “combination of all currently available techniques” which bring them “to the cutting edge of possibilities”.

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