Silver Acetylene Complexes (2)

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Reply**

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ab initio calculations · alkynes · silver ·
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We acknowledge the comments of Krapp and Frenking (KF)[1] on our recent publication "*Homoleptic Silver(I) Acetylene Complexes*"[2] and respond to the issues they raised: KF criticize the use of the term "pseudo-gas phase conditions" as misleading, discussing the difference between solid-state structures and gas-phase structures in HCN–BF_3 and a "high level" (i.e. MP2/def2-SVP)[3] calculated gas-phase structure of pentaphenylborole[4] as examples that intermolecular interactions cannot be neglected. Indeed, the term pseudo-gas phase conditions was only defined for cations in salts with large weakly coordinating anions (WCAs).[5] Such anions separate the cations under investigation considerably and the large, poorly polarizable fluorinated "Teflon"-surface of the anions effectively eliminates interactions between them. Clearly, directed interactions, such as hydrogen bonds and π–π interactions, have a strong influence on the solid-state structures and distort them from the gas-phase geometry. In this respect we agree with KF that there are no pseudo-gas phase conditions in the solid-state structures of HCN–BF_3 and the mentioned borole. However, as detailed analyses of the solid-state structures showed, there are almost no such interactions in the compounds discussed in our publication.[2]

We generally compare the environment provided by salts of good WCAs with the gas-phase conditions inside a mass spectrometer. In agreement with this, we were able to synthesize and characterize compounds in condensed phase that were initially investigated by advanced mass spectrometry (MS) methods, for example, $[Ag(P_4)]^+$, $[Ag(P_4)_2]^+$,[6–8] $[Ag(S_8)]^+$, $[Ag(S_8)_2]^+$,[9,10] $[Cu(CO)_n]^+$ ($n = 1$–4),[11] and CI_3^+.[12–14] In part we were even able to characterize species prior to MS (cf. $[Ag(C_2H_4)]^+$ and $[Ag(C_2H_4)_2]^+$ were identified by MS in 1991,[15] but no evidence for $[Ag(C_2H_4)_3]^+$ was found until 2005;[16] yet $[Ag(C_2H_4)_3]^+[Al(OC(CF_3)_3)_4]^-$ could be prepared in 2003[17]).

The thermodynamic principles of pseudo-gas phase conditions follow from the Born–Haber cycle for the formation of $[AgL_x]^+[A]^-$ ($x = 3, 4$) from $Ag^+[A]^-$ and L ($L = C_2H_2$) for the two differently sized anions $[A]^- = [BF_4]^-$ ($V_{ion} = 0.077\ nm^3$) and the ten-times larger $[Al(OC(CF_3)_3)_4]^-$ ($V_{ion} = 0.758\ nm^3$; Figure 1).[18]

Using volume-based thermodynamics developed by Jenkins and Glasser[20,21] and the molecular volumes of $[Ag(C_2H_2)_3]^+[Al(OR^F)_4]^-$ (**1**) and $[Ag(C_2H_2)_4]^+[Al(OR^F)_4]^-$ (**2**) derived from crystal data ($OR^F = OC(CF_3)_3$), the loss of Gibbs lattice energy upon addition of three C_2H_2 molecules ($\Delta\Delta G_{latt}$) was estimated as only $-48\ kJ\,mol^{-1}$ (and $-15\ kJ\,mol^{-1}$ for the fourth C_2H_2 molecule) in case of the large aluminate anion, but as $-173\ kJ\,mol^{-1}$ (for three) and $-46\ kJ\,mol^{-1}$ (for the fourth) for the tetrafluoroborate (details deposited in the Supporting Information). Only for the large aluminate, the Gibbs energies for the complexation of three or four C_2H_2 molecules are comparable in solid state and gas phase (gas: -260 and $-272\ kJ\,mol^{-1}$ vs. solid: -212 and $-209\ kJ\,mol^{-1}$). The smaller $[BF_4]^-$ ion is much less suited to provide *pseudo*-gas phase conditions; the Gibbs energies for the solid state are greatly reduced to -86 and $-55\ kJ\,mol^{-1}$ and show no resemblance to the gas-phase values. According to the calculated cycle, the gas-phase equilibrium between $[Ag(C_2H_2)_4]^+$, $[Ag(C_2H_2)_3]^+$ and C_2H_2 can easily be calculated [Eq. (1); $p(X)$ is the partial pressure of X; $a(X)$ = activity of $X = p(X)/(1\ atm)$ for an ideal gas].

$$K_{(g)} = \frac{a(AgL_4^+)}{a(AgL_3^+)\,a(L)} = \frac{p(AgL_4^+)\,1\ atm}{p(AgL_3^+)\,p(L)} = e^{-\Delta G^0_{(g)}/RT} = 126 \quad (1)$$
$$\text{with } \Delta G^0_{(g)} = -12\ kJ\,mol^{-1} \text{ at } 298.15\ K$$

Also, the acetylene pressure of solid **2** can be obtained from the equilibrium constant derived from the solid state Gibbs reaction energy ($\Delta G^0_{(s)}$) [Eq. (2)].

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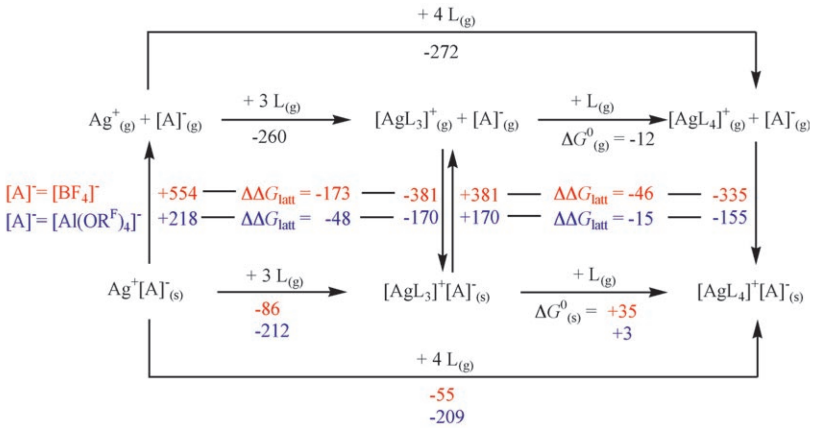

Figure 1. Born–Haber cycle with ΔG^0 values [kJ mol^{-1}] at 298.15 K. Gas-phase reaction energy calculated at MP2(FC)/TZVPP, thermal and entropic corrections at the BP86/SV(P) level (ref. [19]). For solid-state reactions and lattice energies, upper values (red) count for $[A]^- = [BF_4]^-$, lower values (blue) for $[Al\{OC(CF_3)_3\}_4]^-$.

$$K_{(s)} = \frac{a([AgL_4]^+[A]^-{}_{(s)})}{a([AgL_3]^+[A]^-{}_{(s)})\,a(L_{(g)})} = \frac{1}{1\,a(L_{(g)})}$$

$$= \frac{1\ \text{atm}}{p(L)} = e^{-\Delta G^0{}_{(s)}/RT} = 0.29$$

$$p(L) = \frac{1\ \text{atm}}{K_S} = 3.4\ \text{atm} \qquad (2)$$

with $\Delta G^0{}_{(s)} = +3\ \text{kJ mol}^{-1}$ at 298.15 K

for $[A]^- = [Al(OR^F)_4]^-$

The calculated acetylene pressure of 3.4 atm for **2** at 25 °C correlates quite well with the observed decomposition above −20 °C in an atmosphere of acetylene and the need for handling the compounds for sample preparation at temperatures between −50 and −100 °C.

KF calculated the free complexation energy of the fourth acetylene ligand as -11.9 kJ mol^{-1} at −20 °C. While this reproduces our own results quite accurately,[18] we disagree with the interpretation: "This means that free $[Ag(\eta^2\text{-}C_2H_2)_4]^+$ hardly exists in the gas phase". As the *negative* value implies, the reaction is *exergonic* at standard pressures. Using KF's value, the gas-phase equilibrium constant $K_{(g)}$ [see Eq. (1)] is 285 at −20 °C and the ratio between the trisethyne and the tetraethyne complex can be calculated with Equation (3) as 285:1 in C_2H_2 at 1 atm and still 1:1 at 3.5 mbar acetylene pressure.

$$\frac{p([Ag(C_2H_2)_4]^+)}{p([Ag(C_2H_2)_3]^+)} = K_{(g)}\frac{p(C_2H_2)}{1\ \text{atm}} \qquad (3)$$

KF also raise the question whether the experimentally accessible $[Ag(C_2H_2)][A']$ (**3**) model complex[2] ($[A']^- = [Al\{OC(CH)_3(CF_3)_2\}_4]^-$) represents a suitable system to analyze the nature of the acetylene coordination at silver(I) cations under pseudo-gas phase conditions. In fact, we never used the term pseudo-gas phase conditions for **3** and described it explicitly as a molecular model compound in which the anion is clearly coordinating.

KF found on the basis of their own DFT calculations that the free $[Ag(C_2H_2)]^+$ ion displays by 6 pm longer Ag–C bond lengths relative to the corresponding ones calculated in our model system $[Ag(C_2H_2)][A']$ (**3**). They describe the shortening of the Ag–C bond in **3** as "influence of a single counterion". However, the same shortening is calculated[22] in the case of coordinating two neutral water molecules giving $[Ag(H_2O)_2(C_2H_2)]^+$.

Furthermore, KF criticize the agreement between the B3LYP structure calculation of $[Ag(C_2H_2)][A']$ (**3**) and the experimental values as a fortuitous error cancellation. This may well be the case. However, this is a general phenomenon and it is very questionable if intermolecular interactions really contribute to this error cancellation as suggested by KF. In fact, we examined several density functionals and basis sets to find the method that reproduces our experimental results as accurately as possible.[2] Indeed, a broad variation of Ag–C bond lengths was found (221–251 pm), which scatter around the experimental values of 230.7(1) and 230.9(1) pm. The agreement of the "best" method (B3LYP/def2-TZVPP) showing the smallest discrepancies of less than 1 % with regard to the Ag–C, Ag–O, and C–C bond lengths in comparison with the multipolar model, may well be fortuitous. This only accentuates the need for precise structural data from high-resolution X-ray diffraction.

This brings us to the next point—the interpretation of the electronic structure displayed by silver(I) acetylene complexes. According to KF, "the silver–acetylene bond in **3** should be considered as electrostatic". This is a rather strange remark in the light of recent statements published by Nechaev, Rayon, and Frenking (NRF) in 2004: "the nature of the metal–ligand interactions is not very different from each other in the donor–acceptor complexes $[(CO)_5TM{-}C_2H_x]$(TM=Cr, Mo, W), $[(CO)_4TM{-}C_2H_x]$ (TM = Fe, Ru, Os), and $[TM^+{-}C_2H_x]$(TM=Cu, Ag, Au)".[23] Furthermore, NRF stress that "the covalent contributions play an important role" which are characterized by computed stabilizing orbital interaction terms of 41.7 % and 40.6 % (of the attractive interactions) for $[Ag(C_2H_4)]^+$ and $[Ag(C_2H_2)]^+$, respectively.[23] Consequently, NRF revised earlier work of Böhme, Wagener, and Frenking (BWF) in 1996[24a] and of other groups[24b,c] in which "the bonding situation of $[(C_2H_4)TM^+]$ and $[(C_2H_2)TM^+]$ complexes suggested that the interaction is *mainly electrostatic*".[23] It remains unclear which scientific facts led Frenking to change his opinion twice between 1996 and 2008. Indeed, Frenking's present arguments are actually the ones published earlier in 1996 (BWF) which in turn have been criticized by Hertwig et al.[25] in the same year. However, we will show again in the following, that KF's line of argumentation is misleading and in conflict with their own published results and the present literature.

According to KF's calculations the electrostatic nature of the silver–acetylene bond in **3** is reflected by 1) the T-shape of the bond paths, 2) the positive value of the Laplacian ($\nabla^2\rho(\mathbf{r}) = 5.51$ e Å^{-5}), and the small negative value of the energy density ($H(\mathbf{r}) = -0.06$ Hartree Å^{-3}) at the TCP. The TCP represents the bond critical point of the bond path between Ag and the midpoint of the $C{\equiv}C$ bond. We note that the same argumentation has been used 1996 by BWF to classify the bonding in $[Cu(C_2H_x)]^+$ ($x = 2$, 4) as electrostatic "Coulombic interactions". However, on the basis of a personal communication with Frenking, Hertwig et al. could demonstrate in the same year that "increasing the basis set on the ligand to TZP quality, however, also led to a ring structure".[25] Hence, subtle changes in the level of approximation employed might render a T-shape structure of transition-metal π complexes into a metallacyclic one and vice versa. Accordingly, the finding of a T-shape bond path does not rule out the presence of covalency in these type of π complexes. As a natural consequence of both σ donor and π back bonding in these transition-metal π complexes, only small charge-density differences are typically present between the ring and bond critical points in d^{10} configured $[M(C_2H_2)]^{(+)}$ π complexes (M = Group 10 or 11 metal) which render the bond-path graphs rather flexible (see Supporting Information and ref. [26a]). These findings are in line with a recent experimental charge-density work on transition-metal acetylides,[27] where both cyclic and T-shape graphs for ScC_2 moieties were found to co-exist in the solid despite the lack of any significant geometrical differences in the individual ScC_2 moieties.

Also the next two arguments (positive Laplacian and slightly negative $H(\mathbf{r})$ values at the TCP) used by Frenking are misleading. Why should a positive sign of the Laplacian rule out the presence of covalent silver(I) acetylene interactions? KF should more carefully reconcile their arguments with results published earlier by the same group. For example, $[W(CO)_5(C_2H_4)]$, one of Frenking's theoretical prototypes of a Dewar–Chatt–Duncanson (DCD) type olefin complex, displays a positive Laplacian at the W−C bond critical point (BCP) and a slightly negative $H(\mathbf{r}_c)$ value of -0.09 Hartree Å^{-3} (Figure 3 in ref. [28a]). Furthermore, experimental charge-density studies of related textbook examples of DCD-type complexes such as $[Ni(cod)_2]$ (cod = cyclooctadiene)[28b] or $[Ni(C_2H_4)dbpe]$ (dbpe = $t Bu_2PCH_2CH_2P t Bu_2$)[28c] are characterized by positive values at the M–C BCPs (M = transition metal) of +5.6 and +8.4 e Å^{-5}, respectively. We therefore wish to end this controversy once and for all by pointing out that hardly any chemist would classify the carbon monoxide molecule as an electrostatic [C···O] complex lacking covalent bonding because the Laplacian displays a positive value of +23.6 e Å^{-5} at the BCP.[29]

Bader[29] has clearly addressed and carefully investigated these issues over many years. It is therefore not understandable why KF quote in their comment Bader's pioneering work for the wrong reasons. In this respect KF should fully consider the statements given by Bader (page 293 of ref. [29]): "Thus for closed shell interactions, $\rho(\mathbf{r}_c)$ (the charge density at the BCP) is relatively low in value". This clear and simple condition is not fulfilled in the case of **3** and $[Ag(C_2H_2)]^+$ (**3a**). The experimental charge density at the TCP of the 4d^{10} Ag species **3** ($\rho(\mathbf{r}_c) = 0.47$ e Å^{-3}) is somewhat smaller compared to the corresponding value of the DCD-type 4d^{10} Pd complex $[Pd(C_2H_2)]$ (**4**; $\rho(\mathbf{r}_c) = 0.79$ e Å^{-3})[26a], but significantly larger than that of the purely electrostatic π complex $[Na(C_2H_4)]^+$ (**5**; $\rho(\mathbf{r}_c) < 0.1$ e Å^{-3}).[30]

Previous to our work, the electronic structures of $[M(C_2H_x)]^+$ complexes have solely been investigated by theoretical methods. We therefore analyzed the density deformations in the valence shell of the silver atom in **3**[31] to directly reveal the significant role of covalent metal–ligand interactions in $[M(C_2H_x)]^+$ complexes. Indeed, the negative Laplacian ($L(\mathbf{r}) = -\nabla^2\rho(\mathbf{r})$) in the valence shell of the silver atom of **3** reveals a fine structure which is in conflict with "earlier theoretical studies that assumed an electrostatic bonding scenario for silver acetylene complexes".[2] This statement was criticized by KF "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".[1] We could hardly disagree more. Figure 2 shows a comparison of the fine structure of $L(\mathbf{r})$ of the covalent 4d^{10} species **4** and **3a** with that of the reference system $[Rb(C_2H_2)]^+$ (**6**) representing a purely electrostatic 4d^{0}complex employing relativistic all-electron calculations. As a result of our analysis, the electrostatic complex

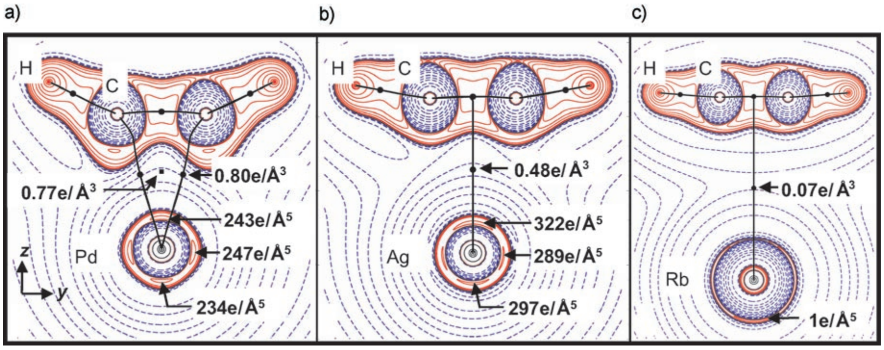

Figure 2. Contour map of the negative Laplacian of the electron density ($L(\mathbf{r}) = -\nabla^2\rho(\mathbf{r})$) of a) **4**, b) **3a**, and c) **6** at the ZORA-BP86/QZV4P level of approximation in the AgC_2 plane. Contour levels are drawn at 0, $\pm 2.0\times10^n$, $\pm 4.0\times10^n$, $\pm 8.0\times10^n$ eÅ^{-5}, where $n = 0, \pm 3, \pm 2, \pm 1$. In the case of **3a** an extra level at 280 eÅ^{-5} has been used while omitting the 200 eÅ^{-5} contour line; positive and negative values are marked by red and blue lines, respectively. RCPs and BCPs are marked by filled squares and circles, respectively, while the bond path is shown by a black line; $\rho(\mathbf{r})$ values at the CPs are specified in [eÅ^{-3}]. The locations of the charge concentrations, the BCPs and TCPs are marked by arrows.

6 shows solely a weak, axial polarization. In contrast, **4** and **3a** reveal a more complex fine structure of the Laplacian showing pronounced charge-depletion zones in the molecular *yz* plane. This is in accordance with the expected charge transfer resulting from the π^*-$(C_2H_2)\leftarrow M(d_{yz})$ ($M = Pd$, Ag) back donation in the framework of the DCD model. Our experimental charge-density study of **3** displays similar charge-depletion zones in the *yz* plane. We further note that the $L(\mathbf{r})$ topology of **3** and model **4** is in good agreement with fully relativistic four-component calculations employing basis sets close to the basis set limit (e.g. Ag/Pd: (33s, 25p, 17d, 9f, 6g, 3h; see Supporting Information). However, as pointed out in our original Communication[2], the π^*-$(C_2H_2)\leftarrow M(d_{yz})$ back donation is less pronounced in the silver complex than in its Group 10 analogues. Accordingly, the acetylene ligand in **4** displays a bonded charge concentration at the carbon atom pointing along the Pd–C directrix which is lacking in the case of **3a** (Figure 2). If we use the magnitude of the bonded charge concentration at the carbon atom to classify the metal atoms with respect to their π^*-$(C_2H_2)\leftarrow M(d_{yz})$ back donation capabilities,[28c] in the $[M(C_2H_2)]^{(+)}$ complexes ($M = Ni$, Pd, Cu^+, Ag^+) the following order can be derived $Ni > Pd > Cu^+ > Ag^+$. This result is in good agreement with the results of the energy decomposition analysis by NRF.[23] Hence, a detailed description of the nature of the M–L bonding in **3** and **3a** has to consider orbital interactions in contrast to the over-simplifying electrostatic picture drawn by KF.

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