DALTON
LETTER

Comments on “T-shaped” 1:1 molecular adducts between chalcogen donors and halogens. Letter and reply

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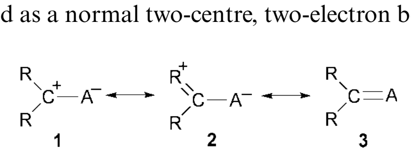
Letter

In a recent paper,[1] a low temperature crystallographic re-investigation of the “T-shaped” 1:1 molecular adduct between *N*-methylbenzothiazole-2-selone (mbts) and Br_2 (mbts·Br_2) was reported. The synthesis of this compound and its X-ray characterisation at room temperature had previously been published by us.[2] However, the authors have justified their structural re-examination by attributing to us an erroneous description of the carbon–selenium bond in this compound. They write: “Additionally, Devillanova *et al.*[2] reported the structure of the T-shaped 1:1 dibromine adduct of mbts for which they described the C–Se linkage as a double bond, with no negative charge on the Br–Se–Br moiety. Hence, these workers felt that a carbene–$SeBr_2$ complex is an appropriate description for this type of adduct, but imply that carbene stabilisation is achieved from substantial back bonding by the $SeBr_2$ moiety to give essentially a carbon–selenium double bond”. Later, in the same paper they write: “if Devillanova’s carbene model for mbts·Br_2 molecule were correct, then C(2) would have a total of five bonds: a double to Se(1), a double to N(1) and a single to S(3)”. In this Letter we wish to clarify our point of view on this type of adduct. Actually, we sketched the mbts·Br_2 adduct with a C=Se bond, but considering the typology of the whole Scheme in which the sketch is included, and especially the reported X-ray crystal structure, it is evident that the sketch should be intended purely as an illustration. Furthermore, we made no comments on the nature of the CSe linkage in mbts·Br_2 except for the following statement: “mbts·Br_2 may be regarded as an adduct of the nucleophilic carbene ligand benzothiazol-2-ylidene with the acceptor $SeBr_2$”.[2] We find it difficult to understand how a double bond nature for the CSe bond in mbts·Br_2 can be inferred from the above statement. In fact, a carbene R_2C: can be seen as an sp^2 carbon atom with one of the hybrid orbitals hosting a lone pair that acts as a σ donor, and the remaining empty p orbital capable of interacting with a π base. An $R_2C{:}\rightarrow A$ adduct between a carbene R_2C: and an acceptor A can be described by several resonance forms considering the $C{:}\rightarrow A$ bond as a normal two-centre, two-electron bond:



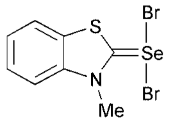
1 2 3

Their relative contribution to the real bonding situation in the adduct depends on the π-donor properties of the substituents A and R at the carbene carbon atom. The resonance structure **2** is expected to be predominant when R has a lone pair located on an orbital perpendicular to the molecular plane, offering the possibility of delocalising the carbon positive charge on a wider π-system (this is the case of mbts·Br_2 or the carbene-pnictinidene adducts recently reported by Arduengo *et al.*[3]). The resonance structure **3** should be important in the case of a back donation from A, as in carbene–metal complexes with the metal in a low oxidation state or in chalcogenone-ligands. Although for carbene–metal complexes the metal–carbon bond distances are generally shorter than those corresponding to an M–C single bond, as found in alkyl-complexes, they are much longer than in the carbonyl complexes, suggesting a limited double bond M=C character.[4] Many chalcogenone-ligands, similar to mbts, have actually been synthesized by reacting stable carbenes with elemental chalcogens.[5] In these cases, the back donation occurs from the symmetry-appropriate p orbital on A to the empty p orbital on C and the resonance structure **3** becomes predominant. Consequently, the sentence in ref. 1 “It would appear, therefore, that disagreement exists as to the exact structural nature of these T-shaped adducts, *i.e.* ‘purely’ carbene *versus* ‘purely’ zwitterionic forms” is wrong, because a carbene–acceptor interaction could lead to a bonding situation ranging from a single to a double bond. On the other hand, according to the VSEPR model,[6] if the acceptor is an AX_2E_2 species (A = chalcogen, X = halogen, E = lone pair), its carbene-adduct is bound to have a “T-shaped” geometry resulting from a trigonal bipyramidal arrangement of five electron pairs around the central chalcogen, with the two lone pairs occupying equatorial positions. Clearly, for an $R_2C{:}\rightarrow AX_2E_2$ adduct, the lone pairs (E) have not the appropriate symmetry to act as π-donors towards the empty p orbital of the carbon. Therefore, in our opinion the description of mbts·Br_2 as a carbene–$SeBr_2$ adduct implies a single bond rather than a double bond character for the C–Se linkage.

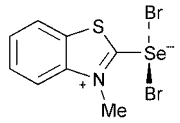
We wish to conclude with a few remarks: (1) our structure at room temperature is more precise [$R = 0.034$, $R_{int} = 0.019$, 1578 reflections with $I > 3\sigma(I)$][2] than at −70 °C [$R = 0.076$, $R_{int} = 0.1110$, 4181 unique reflections with $I > 2\sigma(I)$],[1] and as expected, both exhibit identical C–Se bond distances (within 3σ). Therefore, any discussion about different bond distances for both structures (mostly due to packing effects) is hampered. (2) Surprisingly, the authors of ref. 1 consider it correct to describe an adduct related to mbts·Br_2, and reported by Williams *et al.*,[7] as “a stable aromatic heterocycle carbene complex of selenium(II) bromide”. Is it because Williams *et al.*[7] have explicitly stated that the C–Se linkage has a single bond character or is it perhaps because they have schematically drawn the adduct in a zwitterionic form? (3) It should not be forgotten that many similar compounds are actually prepared by reacting stable carbene species with appropriate acceptors of the type AX_2E_2.[8] (4) In a subsequent paper[9] we dealt with the interaction of mbts with Br_2 on an experimental basis. The reported reaction mechanism clearly shows the adduct in its "T-shaped zwitterionic structure" but these results, which clarify our vision of the bond in mbts·Br_2, have not been considered.

Reply

We thank Professor Devillanova and his group for their comments. Two ways of representing mbts·Br_2 are (**a**) as it appeared in their two *Polyhedron* papers[2,9] and (**b**) as described recently by us.[1]



(**a**)



(**b**)

This molecule was described in their text as a carbene–acceptor adduct: a view we broadly accept. However, because the CSe linkage is represented in (**a**) as a double bond, the implication is that the structure exists predominantly in resonance form **3**; this would necessarily require substantial back-donation from the $SeBr_2$ moiety. We pointed out[1] that this did not fit the data and that it seems far more likely that lone-pair donation from the nitrogen atom is favoured over back-donation from an $SeBr_2$ acceptor, making resonance **2** the predominant form. A discussion of bond lengths, charge separation and the zwitterionic nature of mbts·Br_2 was not included in their report[2] prompting us to undertake a reexamination of the data (including a low-temperature single crystal reanalysis) which formed a small part of our paper[1] dealing with four structures arising from the interaction of selenoamides with dibromine. A comparison of the precision of the two structures is not necessary as we wished merely to increase the quantity of data available (especially concerning the CSe and CN distances) in order to be certain our interpretation was correct.

Examination of both sets of XRD data, in addition to the ^{13}C NMR data we presented, shows incontrovertibly that the CSe linkage is single and that the CN bond is double. This is in direct disagreement with their representation (**a**).[2,9] We then went on to discuss our interpretation of the structure (**b**) in two ways; as a carbene (of form **2**) and as a zwitterion. We did not negate the role of carbenes in similar systems[5,8] but pointed out that similar molecules described by Akabori *et al.* can only be thought of as zwitterions.[10] Hence, we simply stated that a carbene model is not always appropriate and perhaps should not be automatically invoked. We in fact did *not* describe Williams' structure as "a stable aromatic heterocycle carbene complex of selenium(II) bromide"; careful reading of the text[1] would have shown that this is how Williams described it himself. Nevertheless, his representation (as a carbene predominantly of resonance form **2**) was indeed entirely valid on the basis of the data he presented.[7] However, Devillanova's representation of the structure of mbts·Br_2 (**a**) was not.

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