

Dimethylargenate is a stable species in the gas phase

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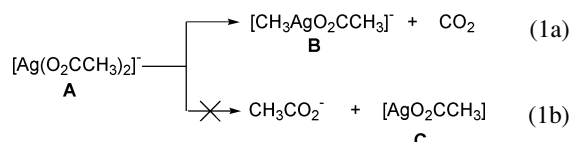
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The formation of dimethylargenate from silver diacetate has been explored using multistage mass spectrometry experiments in a quadrupole ion trap and DFT theory.

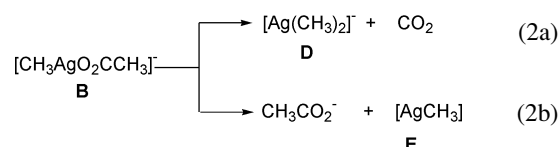
While organocopper reagents such as lithium diorganocuprates are widely used in organic synthesis,¹ related organosilver reagents have received much less attention due to their lower thermal stability and photosensitivity.² This contrast is nicely illustrated for the simplest (dialkyl)M(I) species: the $[\text{Cu}(\text{CH}_3)_2]^-$ anion has been characterized by X-ray crystallography,³ but the related $[\text{Ag}(\text{CH}_3)_2]^-$ anion has not been reported.⁴ Inspired by a report which described the gas phase synthesis of deprotonated phenyllithium and phenylsodium species from carboxylate precursors,⁵ this communication examines the gas phase formation of organosilver species^{6,7} from silver diacetate using a combination of multistage mass spectrometry experiments in a quadrupole ion trap⁸ and DFT theory.⁹

Electrospray ionisation of silver(I) acetate in the negative ion mode results in several silver containing anions, the most abundant of which corresponds to $[\text{Ag}(\text{O}_2\text{CCH}_3)_2]^-$ **A**.¹⁰ Collision induced dissociation (CID) of **A** results in loss of CO_2 to yield $[\text{CH}_3\text{AgO}_2\text{CCH}_3]^-$ **B**, as the only charged species [eqn. (1a)].^{11,12} Loss of acetate anion to yield neutral silver acetate $[\text{AgO}_2\text{CCH}_3]$ **C**, is not observed [eqn. (1b)]. This is quite



surprising since eqn. (1b) represents a single heterolytic bond cleavage reaction of a Ag–O bond, while eqn. (1a) requires both Ag–O and C–C bond cleavage reactions with transfer of the CH_3 group to Ag. An examination of the collision induced dissociation (CID) MS^3 spectrum of **B** shown in Fig. 1 reveals the presence of two competing fragmentation pathways: loss of CO_2 to form $[\text{Ag}(\text{CH}_3)_2]^-$ **D** [eqn. (2a)], as well as the loss of acetate anion to yield neutral methylsilver $[\text{AgCH}_3]$ **E**, [eqn.

(2b)]. The novel organosilver ions **B** and **D** are both stable in the gas phase and can be isolated for periods of 10 seconds without decomposition.



In order to gain further insights into the processes shown in eqns. (1) and (2), DFT calculations have been carried out on each of the neutral and charged species.¹³ Structures of the silver containing species **A–D** are shown in Fig. 2, while the energies and zero point vibrational energies (ZPVE) of all species are listed in Table 1. To evaluate possible precursors to CO_2 loss from **B**, two conformers around the C–O bond were optimized, and these are shown as **B1** and **B2**. Each of the dicoordinate silver anions **A**, **B** and **D** are close to linear, with **B1** deviating the furthest from linearity (with a C–Ag–O bond angle of 174.4°). The CH_3 –Ag bond length in **E** is consistent

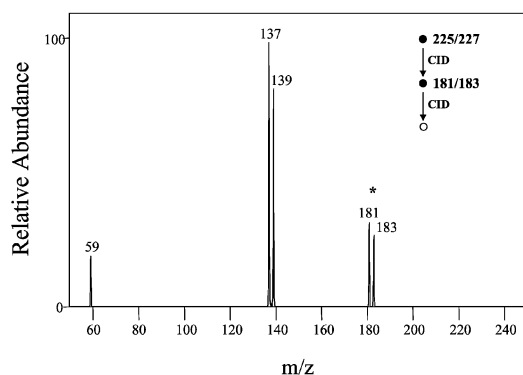


Fig. 1 MS^3 spectrum showing the fragmentation of $[(\text{CH}_3)\text{Ag}(\text{CH}_3\text{CO}_2)]^-$, which is designated by an asterisk.

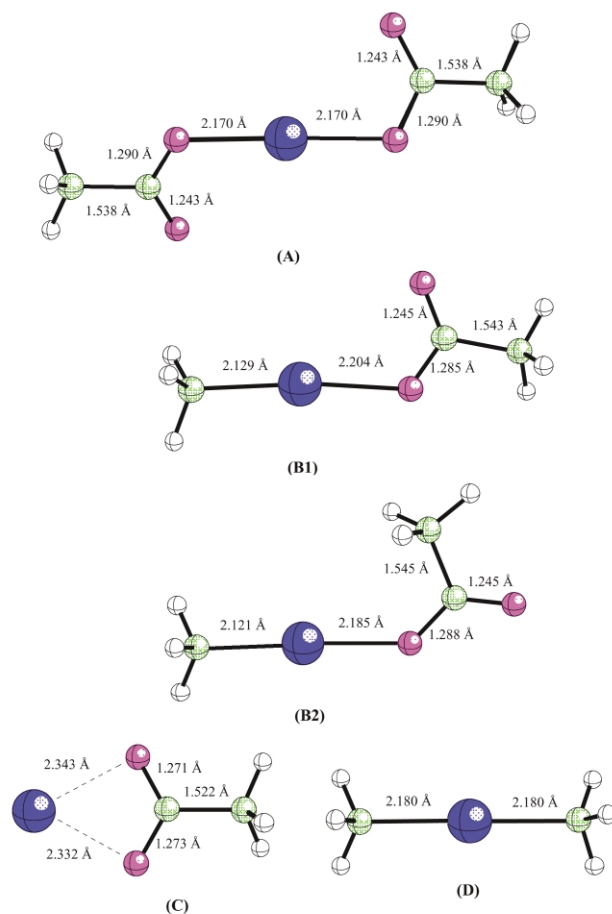


Fig. 2 DFT optimized structures of the silver species **A–D**.

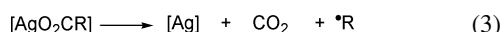
Table 1 Results from DFT calculations on neutral and charged species shown in eqns. (1)–(4)

Species	B3LYP/6-31+G* ^a	B3LYP/6-31+G* ZPVE ^{ab}
[Ag(CH ₃ CO ₂) ₂] [−] A	−602.88874	0.10030
[(CH ₃)Ag(CH ₃ CO ₂)] [−] B1	−414.25797	0.08449
[(CH ₃)Ag(CH ₃ CO ₂)] [−] B2	−414.25578	0.08464
[Ag(CH ₃ CO ₂) ₂] C	−374.26925	0.05024
[Ag(CH ₃) ₂] [−] D	−225.61078	0.06757
[Ag(CH ₃) ₃] E	−185.66276	0.03499
CO ₂	−188.58597	0.00960
CH ₃ CO ₂ [−]	−228.53574	0.04813

^a Energies are in Hartrees. ^b Uncorrected ZPVE.

with previous calculations.¹⁴ Furthermore, the increase in CH₃–Ag bond length on going from the neutral **E** (2.130 Å) to the anion **D** (2.180 Å) follow the same trend observed for the related copper species.¹⁴ One of the more unusual structures is the neutral **C**, in which the acetate ion binds as a bidentate ligand to the silver ion. The Ag–O bond lengths are not equivalent, and the shorter Ag–O bond is still significantly longer than the Ag–O bond in either **A** or **B**. Perhaps the most interesting results concern the DFT predicted energetics for eqns. (1) and (2). Firstly, the conformer **B1** is more stable than **B2** by only 1.5 kcal mol^{−1}. Reaction (1a) (endothermic by 24.3 kcal mol^{−1}) is clearly favoured over reaction (1b) (endothermic by 51.4 kcal mol^{−1}). In contrast reaction (2b) (endothermic by 36.5 kcal mol^{−1}) is energetically competitive with reaction (2a) (endothermic by 33.9 kcal mol^{−1}). Thus the DFT predicted precursor and product energetics nicely confirm the experimentally observed fragmentation reactions for **A** and **B**.

How do these results compare with related solution phase processes? The thermal decomposition reactions of metal carboxylates in the condensed phase are quite complex,^{15a} although successful applications to the synthesis of organometallics *via* decarboxylation reactions have been reviewed.^{15b} Some success with silver perfluorocarboxylates has been noted,^{16a,b} but this thermal decomposition pathway is not the only one available in solution, with other silver carboxylates often fragmenting *via* radical formation [eqn. (3)].^{16c}



Further work is underway to examine the gas phase formation and reactivity of other alkyl and aryl silver anions, and to test the generality of CO₂ loss from charged metal carboxylates in the gas phase.

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- All experiments were carried out using a Finnigan LCQ quadrupole ion trap mass spectrometer. Electrospray solutions were made to 0.1 g mL^{−1} in MeOH. Typical ESI conditions: Sheath gas flow rate 60 (arbitrary units), auxiliary gas flow rate 0 (arbitrary units), spray voltage 5 kV, capillary temp. 100 °C, capillary voltage −5 V, tube lens offset −5 V. Multistage mass spectrometry experiments were carried out using the advanced scan function of the LCQ. Both Ag isotopes were mass selecting with a window of 5 Da for the ions of interest and subjected to collision induced dissociation using the following conditions: an activation *Q* of 0.2 (to allow detection of acetate ion at *m/z* 59), voltage of 0.6 and activation time of 30 ms.
- CO₂ loss has also been used to examine the formation and reactivity of alkyl anions from carboxylate anions in the gas phase. For a lead reference, see: R. R. Squires, *Acc. Chem. Res.*, 1992, **25**, 461.
- A referee has correctly pointed out that the first decarboxylation reaction does not necessarily require formation of an Ag–C bond, as other isomeric products are possible. Attempts to locate an adduct formed *via* attack of a methyl anion onto the O atom of silver acetate *via* DFT calculations (see ref. 13) resulted in fragmentation of the silver complex and concomitant formation of methylacetate. In contrast, an adduct [Ag(O₂C(CH₃)₂)][−], formed *via* attack of the methyl anion onto the C atom of silver acetate was located, but it is less stable than **B1** by >50 kcal mol^{−1}.
- DFT calculation were carried out at the B3LYP level of theory using a 6-31 + G* basis set for C, H and O and a LANL2DZ pseudo potential for Ag. Optimizations were carried out without any symmetry constraints. Vibrational frequency calculations were carried out on each optimized structure at the same level of theory. Reaction energetics were calculated by using the energies listed in Table 1, with the ZPVE corrected by 0.9806 (A.P. Scott and L. Radom, *J. Phys. Chem.*, 1996, **100**, 16502). A similar basis set has been shown to yield reasonable dissociation energies: C. K. Kim, J. Won, H. S. Kim, Y. S. Kang, H. G. Li and C. K. Kim, *J. Comput. Chem.*, 2001, **22**, 827.
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