A copper(I)-catalysed template synthesis of solvatochromic aryl-arsonium and -stibonium systems and a synchrotron structural study of a tetraarylstibonium di-iodocuprate

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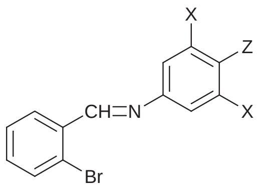
A route to solvatochromic tetraaryl-arsonium and -stibonium phenolate betaines is described, together with a synchrotron structural study of a precursor arylstibonium di-iodocuprate salt in which both cation and anion have unusual geometries.

Methods for the synthesis of aryl-arsonium or -stibonium salts from tertiary arsines or stibines and aryl halides are limited, the usual route being the reaction of the tertiary arsine or stibine, commonly the triphenyl derivative, and an aryl halide, in the presence of aluminium chloride at > 200 °C.[1] We have shown that tertiary phosphines react with aryl halides bearing appropriate donor atoms in the *ortho* position to the halogen in the presence of catalytic quantities of nickel(II) or copper(II) compounds under mild conditions in refluxing ethanol,[2] and were interested in exploring similar template-assisted reactions of triaryl-arsines and -stibines. As triaryl-arsines and -stibines coordinate readily to copper(I) halides to form complexes which are labile in solution,[3] we have investigated their reactions with a series of template aryl halides in the presence of copper(I) iodide, in acetonitrile, and wish to report the formation of tetraaryl-arsonium and -stibonium systems in high yield under these remarkably mild conditions. We have also applied this procedure in the synthesis of the first solvatochromic tetraarylarsonium and -stibonium iminophenolate betaines, the properties of which are compared with those of the related phosphonium system. A synchrotron structural study of one tetraarylstibonium salt is also reported, which reveals a significant intramolecular coordinative interaction between the onium centre and the donor atom in the *ortho* position of the template system, and also the presence of a di-iodocuprate(I) anion which interacts with a second di-iodocuprate anion *via* a short copper–copper interaction to give a dinuclear anion.

The reaction of the aryl halides **1** (X = H, Z = OMe; X = Cl, Br, or Ph, Z = OH) with triphenylarsine and copper(I) iodide in acetonitrile under reflux for several hours gave, after pouring into aqueous potassium iodide solution and solvent extraction into dichloromethane, the tetraarylarsonium salts **2** (E = As, Y = I or CuI_2) as yellow-brown crystalline solids. ^{1}H and ^{13}C NMR spectra were consistent with the proposed structures. Under FABMS conditions, the arsonium salts gave a characteristic molecular ion for the cation present. The structure of the salt **2** (X = H, Z = OMe, E = As, Ar = Ph, Y = I) was also confirmed by a full X-ray crystallographic study.[4] Similarly, treatment of the aryl halides **1** (X = H, Z = OMe; X = Cl, Br, or Ph, Z = OH) and **3** with triphenyl- or tri-*p*-tolyl-stibine and copper(I) iodide in acetonitrile under reflux gave the related arylstibonium salts **2** (E = Sb; Ar = Ph or *p*-tolyl, Y = CuI_2) and **4** (Ar = Ph or *p*-tolyl, Y = CuI_2). Again, ^{1}H and ^{13}C NMR spectra were consistent with the proposed structures, and under FABMS conditions, each stibonium salt gave a characteristic molecular ion for the cation present. The nature of the anion present was confirmed by negative ion mass spectrometry. The stibonium salts formed more quickly than the related arsonium salts under the same conditions. Attempts to prepare the related phosphonium salts using copper(I) iodide as catalyst in acetonitrile were unsuccessful. Clearly, the group 15 ligand must influence crucial stages of the reaction, for which the mechanism is uncertain. A kinetic study of related nickel(II)-catalysed reactions of phosphines with template aryl halides supported a mechanism in which oxidative insertion of an intermediate phosphine–nickel complex into the carbon–halogen bond was the key step, followed by reductive elimination of the arylphosphonium salt and regeneration of the effective catalyst.[5] It is likely that a similar mechanism applies in the above reactions, perhaps involving a copper(I)–copper(III) redox cycle, in which the triaryl-arsine and -stibine ligands are able to stabilise intermediate organometallic species more effectively than the related triarylphosphines.



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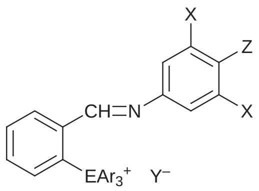

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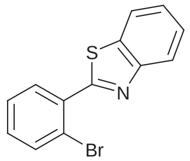

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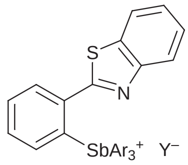

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A structural study‡ has been made of the stibonium salt **2** (E = Sb; Ar = Ph; X = Br; Z = OH, Y = CuI_2). Routine investigations, using a rotating anode X-ray source, failed to provide data of sufficient intensity to produce a fully refinable structure. Data were therefore collected, upon a crystal of dimensions 200 × 20 × 20 μm, using station 9.8 of the Daresbury SRS.[6] The cation of the observed structure is displayed in Fig. 1 (together with selected bond lengths and angles for both cation and anion). Significant points of interest are the close intramolecular approach of the imino nitrogen to the stibonium centre, the antimony–nitrogen distance (2.65 Å), lying well within the sum of the van der Waals' radii (3.75 Å),[7] and the consequent distortion of the bond angles at antimony from the idealised tetrahedral angle towards a five-coordinate arrangement, consistent with an intramolecular coordinative interaction from nitrogen to antimony to form a five-membered ring. Tetraarylstibonium halides also show considerable distortion from idealised tetrahedral geometry as a result of weak interactions of the stibonium centre with the halide ion, resulting in essentially trigonal bipyramidal structures in which the antimony–halogen bond is unusually long.[8,9] The structure co-crystallises with a 50% occupied CH_2Cl_2 solvent and the counter-ion, which was found to be di-iodocuprate(I). The CuI_2

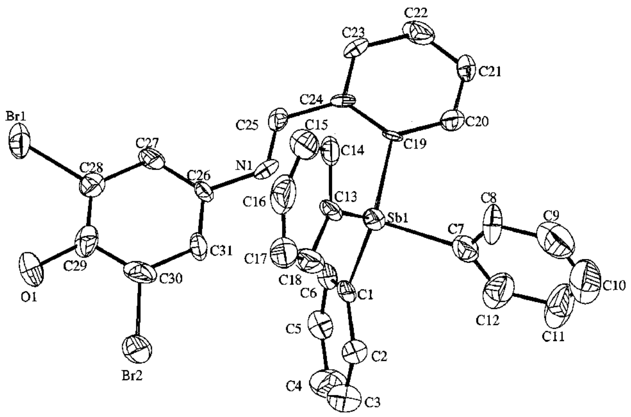
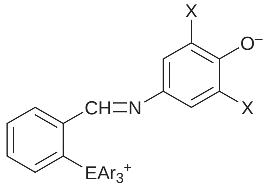


Fig. 1 Structure of the tetraarylstibonium cation with selected bond lengths (Å) and angles (°) for cation and di-iodocuprate anion: Sb–N1 2.65(4), Sb–C1 2.09(2), Sb–C7 2.13(2), Sb–C13 2.13(2), Sb–C19 2.114(14), C25–N1 1.28(2), Cu1–I1 2.508(2), Cu1–I2 2.576(2), Cu–Cu 2.732(4); C1–Sb–C7 106.7(7), C1–Sb–C13 119.2(6), C1–Sb–C19 113.6(6), C7–Sb–C13 102.0(7), C7–Sb–C19 101.4(6), C13–Sb–C19 115.9(6), C19–C24–C25 121.2(14), N1–C25–C24 118.9(13), N1–Sb–C1 83.9(7).

moiety shows a considerable distortion from the expected linear arrangement as a result of a very short copper–copper interaction (2.73 Å) with a second di-iodocuprate anion in the lattice. The stabilisation of poly[dihalocuprate(I)] anions by large phosphonium cations has been documented,[10,11] but the only stibonium salt involving a related anion is that of the copper(II) complex, $(SbPh_4)_2\cdot Cu_2Cl_6$.[12] However the Cu–Cu separation in this structure is much greater (3.394 Å) than that in the di-iodocuprate(I) counter-ion discussed here. Comparison with other di-iodocuprate(I) anions crystallizing in the same manner shows the Cu–Cu separation to be somewhat greater than in our example (average = 2.95 Å).[13,14]

Treatment of the salts **2** (E = As or Sb; Ar = Ph; X = Cl, Br, or Ph), dissolved in dichloromethane, with aqueous sodium hydroxide solution, resulted in a marked colour change from yellow to red-purple with formation of the related betaines **5**,



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which were subsequently isolated and purified by trituration with diethyl ether. Again, ^1H and ^{13}C NMR spectra were consistent with the proposed structures, showing some significant chemical shift changes compared to the parent salts. Under FABMS conditions, cationic molecular ions were again observed. Conversion to the betaines resulted in a significant shift of the visible absorption maximum to longer wavelength. Thus, *e.g.* λ_{max} for the salt **2** (E = Sb; Ar = Ph; X = Cl, Y = CuI_2) in dichloromethane was observed at 358 nm, whereas for the related betaine **5** in the same solvent, λ_{max} = 536 nm. Significantly, in view of the potential link with non-linear optical properties, the betaines exhibited negative solvatochromism, the visible absorption maximum moving to longer wavelength on moving to a solvent of lower polarity. In the case of the above betaine, λ_{max} moved from 536 nm in dichloromethane to 576 nm in THF. The solvatochromic behaviour of the arsonium and stibonium betaines is almost identical to that of the related phosphonium betaines **5** (E = P, Ar = Ph; X = Cl, Br, or Ph) which we reported recently.[15] There is currently growing interest in the optical properties of organic derivatives of the main group 15 elements.[16,17]

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Notes and References

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‡ *Crystal data*: $C_{31.5}H_{23}NOClSbBr_2\cdot CuI_2$, M_r = 1065.87, monoclinic, space group $P2_1/n$, a = 9.259(5), b = 24.785(11), c = 15.100(7) Å, β = 98.998(2)°, U = 3422.6(3) Å^3, Z = 4, D_c = 2.069 g cm^{-3}, μ = 5.653 mm^{-1}, $F(000)$ = 2000, crystal size 0.2 × 0.02 × 0.02 mm. Data were collected at 160 K, with a wavelength of 0.6875 Å, on a Bruker (formerly Siemens) SMART CCD area detector diffractometer, equipped with a silicon(111) crystal monochromator and a palladium coated focussing mirror on station 9.8 of the Daresbury SRS. ω scans, with a frame increment of 0.3°, were used to cover a hemisphere of reciprocal space, giving θ_{min} = 1.54° and θ_{max} = 20.00° (index ranges $-11 \leqslant h \leqslant 12$, $-26 \leqslant k \leqslant 32$, $-18 \leqslant l \leqslant 19$). Corrections were applied to account for incident beam decay and absorption effects. A solution was obtained *via* direct methods and refined by full-matrix least-squares on F^2. 3520 unique data were produced from 11707 measured reflections (R_{int} = 0.0882). 389 parameters refined to R_1 = 0.0573 and wR_2 = 0.1253 [$I > 2\sigma(I)$] with s = 1.057 and residual electron densities of 0.967 and −1.124 e Å^{-3}. CCDC 182/984.

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