JOURNAL OF
Materials
CHEMISTRY

A copper(I)-catalysed template synthesis of aryl-arsonium and -stibonium systems. Solvatochromic tetraaryl-arsonium and -stibonium iminophenolate betaines

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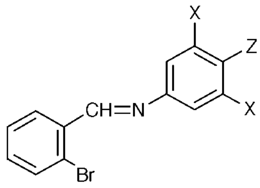
Received 23rd September 1999, Accepted 1st December 1999

A series of aryl-arsonium and -stibonium salts bearing an imino substituent in the *ortho* position to the cationic centre has been prepared by the reactions of *ortho*-halogenoarylimines with triaryl-arsines and -stibines in the presence of copper(I) iodide in acetonitrile. X-Ray crystal structural studies reveal the existence of intramolecular coordination from the imino nitrogen to arsenic and antimony, with consequent distortion of bond angles about the group 15 element, which adopts a trigonal bipyramidal structure. Deprotonation of arsonium and stibonium salts derived from *ortho*-halogenoaryliminophenols gives a series of highly coloured aryl-arsonium and -stibonium iminophenolate betaines, which have been shown to exhibit a significant degree of negative solvatochromism, similarly to their previously reported arylphosphonium analogues. The visible absorption properties and solvatochromism are largely independent of the nature of the group 15 element, implying little d-orbital contribution to bonding in either ground or excited states.

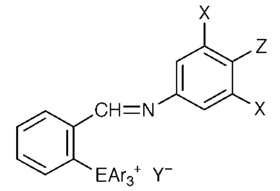
Introduction

There is currently growing interest in the properties of the organic derivatives of the heavier main group 15 elements as opto-electronic materials.[1,2] We have recently described the synthesis of series of dipolar phosphonioaryl-imidazolide and phosphonioaryl-phenolate betaine systems, which were found to exhibit negative solvatochromism.[3,4] Compounds which are solvatochromic are also of potential interest in that they may also exhibit non-linear optical properties under appropriate circumstances. We have therefore extended our studies in the above area to include a comparison of the properties of the related arsonium and stibonium dipolar systems.

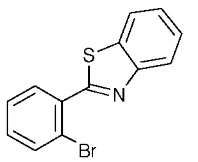
Methods for the synthesis of aryl-arsonium or -stibonium salts from tertiary arsines or stibines and aryl halides are limited, the usual route being the reaction of the tertiary arsine or stibine, commonly the triphenyl derivative, and an aryl halide, in the presence of aluminium chloride at >200 °C.[5] 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,[6] 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,[7] we have investigated their reactions with a series of template aryl halides in the presence of copper(I) iodide, in acetonitrile, and 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 tetraaryl-arsonium and -stibonium iminophenolate betaines, the properties of which are compared with those of the related phosphonium system. X-Ray structural studies of representative compounds are also reported, and reveal significant intramolecular coordinative interactions between the 'onium centre and the donor atom in the *ortho* position of the template system. A preliminary report of this work has been published.[8]



1 X = H, Cl, Br or Ph
Z = OH or OMe



2 E = As or Sb; X = H, Cl, Br or Ph
Z = OH or OMe
$Y = I^-$ or CuI_2^-



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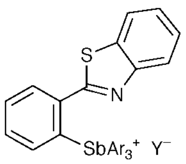

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Results and discussion

Formation of aryl-arsonium and -stibonium salts

The reaction of aryl halides **1** ($X = H$, $Z = OMe$, $X = Cl$, Br, 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 related tetraarylarsonium salts **2** ($E = As$, $Ar = Ph$) as yellow–brown crystalline solids. ^1H NMR spectra were consistent with the proposed structures. Under high resolution FAB MS conditions, the arsonium salts gave a

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characteristic molecular ion for the cation present. The structure of the salt **2** (E = As, Ar = Ph, X = H, Z = OMe, Y = I) was also confirmed by a full X-ray crystallographic study (*vide infra*). Similarly, treatment of the aryl halides **1** (X = H, Z = OMe, X = Cl, Br, 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, *p*-tolyl) and **4** (Ar = Ph, *p*-tolyl). Again, ^{1}H NMR spectra were consistent with the proposed structures, and under high resolution FAB MS conditions, each stibonium salt gave a characteristic molecular ion for the cation present. The nature of the associated anion varied in both series of salts and was somewhat problematical. While some arsonium salts, *e.g.* **2** (E = As, Ar = Ph, X = H, Z = OMe, Y = I) were isolated as simple 'onium iodides, others involved a mixture of iodide and diiodocuprate anions, and some were isolated solely as diiodocuprates. The related stibonium salts were isolated predominantly as diiodocuprates, although some clearly contained a mixture of iodide and diiodocuprate anions. Solutions of some of the 'onium diiodocuprates in dichloromethane or deuteriochloroform gradually became cloudy, owing to precipitation of cuprous iodide. Evidence of the nature of the anion(s) present was adduced by determination of the copper content, and also by negative ion mass spectrometry, often revealing the presence of the diiodocuprate ion of mass 317. 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.[9] 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.

Structural studies

In the preliminary report of this work,[8] we described an X-ray structural study of the arylstibonium salt **2** (E = Sb, Ar = Ph, X = Br, Z = OH, $Y = CuI_2$). Significant points of interest were the close intramolecular approach of the sp^2-hybridised imino nitrogen to the stibonium centre, the antimony–nitrogen distance (2.65 Å) lying well within the sum of the van der Waal's radii (3.75 Å),[10] 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. There was no close approach to antimony of either iodine atom present in the diiodocuprate anion, in contrast to the observed interaction of halide ions with the cationic centre of simple tetraarylstibonium salts, resulting in essentially trigonal bipyramidal structures in which the antimony–halogen bond is unusually long.[11,12] A full X-ray structural study has now been made of the related arsonium salt **2** (E = As, X = H, Z = OMe, Y = I).

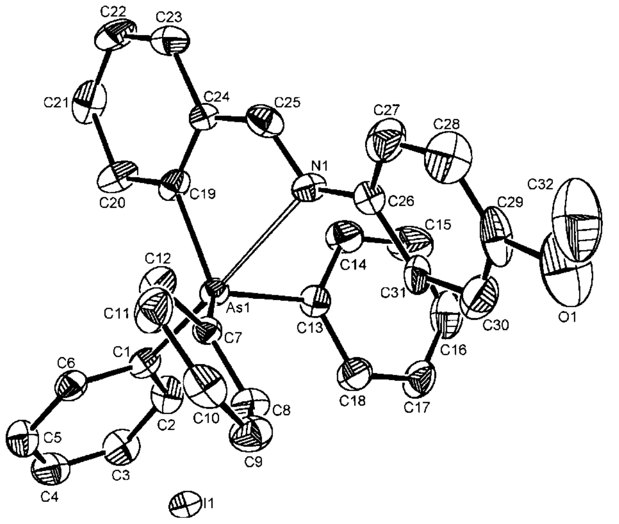
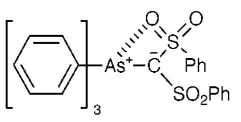


Fig. 1 Solid-state structure of *N*-[(2-triphenylarsoniobenzylidene)]-1-amino-4-methoxybenzene iodide, showing the atom labeling scheme. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level.

The solid state structure of the arsonium salt is displayed in Fig. 1, and selected bond lengths and angles are given in Table 1. The structure consists of $[Ph_3As(C_6H_4CH{=}NC_6H_4\text{-}OMe)]^+$ cations and I^- anions held together by weak electrostatic interactions. The shortest cation–anion contacts are I(1)···(3) 3.28 Å and I(1)···H(21) ($-1+x$, y, z) 3.22 Å. As with the above stibonium salt, we note the close approach of the imino nitrogen to the arsonium centre, the arsenic–nitrogen distance (2.772 Å), lying well within the sum of the van der Waal's radii (3.40 Å),[10] and the consequent distortion of the bond angles at arsenic from the idealised tetrahedral angle towards a five-coordinate arrangement, again consistent with an intramolecular coordinative interaction from nitrogen to arsenic to form a five-membered ring. The coordination geometry around the arsenic atom may be described as distorted trigonal bipyramidal, with a nearly linear apical axis [C(1)–As(1)–N(1) 173.4°]. The iodide anion does not interact with the arsonium centre, as is also the case in simple tetraarylarsonium salts,[13,14] in contrast to that observed in related stibonium systems as noted above. While there do not appear to be any structural data to compare for related *ortho*-substituted phenylarsonium salts, a similar intramolecular coordinative interaction (albeit forming a four-membered ring) has been observed in triphenylarsonium bis(phenylsulfonyl)-methylide **5** and triphenylarsonium 4,4-dimethyl-2,6-dioxo-cyclohexylylide **6**.[15] It is perhaps of interest that in the above arsonium and stibonium salts, the antimony–nitrogen distance (2.65 Å) is shorter than the related arsenic–nitrogen distance (2.772 Å), despite the greater atomic radius of antimony, indicating a stronger coordinative interaction for the antimony system. A similar observation has been made regarding the antimony–oxygen distance in the stibonium analogues of the ylides **5** and **6**.[15] The bond lengths and angles associated with the ligands are as expected. A value of 3.5(10)° for the C(25)–N(1)–C(26)–C(27) torsion angle shows that the methoxy-substituted phenyl ring is nearly coplanar with the –CH=N– bridge, whilst the C(19)–C(24)–C(25)–N(1) torsion angle at 17.5(11)° indicates considerable strain owing to chelate formation. This is an additional evidence for a 'bonding' interaction of N(1) with the arsenic centre.



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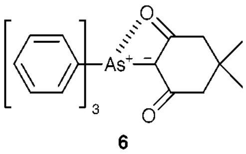

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Betaine formation and solvatochromism

Treatment of the salts **2** (E = As, Sb; Ar = Ph; X = Cl, Br, Ph; Z = OH), dissolved in dichloromethane, with aqueous sodium hydroxide solution resulted in a marked colour change from

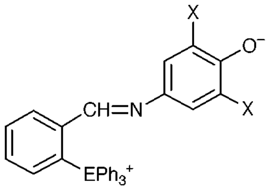
Table 1 Selected bond angles (°) and bond lengths (Å) for *N*-[(2-triphenylarsoniobenzylidene)]-1-amino-4-methoxybenzene iodide **2** (E = As, X = H, Z = OMe, Y = I)

C(1)–As(1)–C(7)	103.7(3)	C(19)–C(24)–C(25)	123.7(6)
C(1)–As(1)–C(13)	105.2(3)	N(1)–C(25)–C(24)	119.6(6)
C(1)–As(1)–C(19)	107.1(3)	N(1)–As(1)–C(1)	173.4(4)
C(7)–As(1)–C(13)	118.0(2)	N(1)–As(1)–C(7)	70.6(4)
C(7)–As(1)–C(19)	113.1(3)	N(1)–As(1)–C(13)	80.9(4)
C(13)–As(1)–C(19)	108.7(3)	N(1)–As(1)–C(19)	72.8(4)
As(1)–N(1)	2.772(7)	As(1)–C(13)	1.925(7)
As(1)–C(1)	1.924(7)	As(1)–C(19)	1.925(6)
As(1)–C(7)	1.902(6)	C(25)–N(1)	1.276(7)

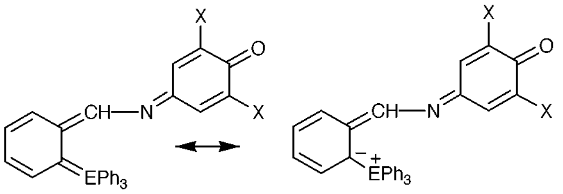
yellow to red–purple with formation of the related betaines 7**A**, which were subsequently isolated and purified by trituration with diethyl ether. Again, ^{1}H NMR spectra were consistent with the proposed structures, showing some significant chemical shift changes compared to the parent salts (Table 2). Under high resolution FAB MS conditions, cation 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, Z = OH) in dichloromethane was observed at 358 nm, whereas for the related betaine 7**A** in the same solvent, $\lambda_{max} = 536$ nm. Significantly, 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 7**A** (E = P, Ar = Ph; X = Cl, Br, Ph) which we reported recently.[4] Full details of the solvatochromic properties of the betaines are presented in Table 3, and comparative data for the precursor 'onium salts in Table 4. Significantly, the latter do not show any significant solvatochromic properties. Clearly, in the betaines, the negative charge of the phenolate system is delocalised over the conjugated system, aided by the polarising effect of the arsonium or stibonium centre. The observation of negative solvatochromism, as with the related phosphonioiminophenolates,[4] reflects the stabilisation in the more polar solvents of the ground state dipolar betaine form 7**A** relative to less polar excited state forms, *e.g.*, 7**B** and 7**C**, of which the dipolar ylidic form 7**C** would be expected to be dominant, in view of the minimal d-orbital involvement in the bonding in formally pentacovalent but four-coordinate (λ^5, σ^4) main group 15 compounds.[16] The great similarity in the solvatochromism of the phosphonium, arsonium and stibonium betaines also suggests that d-orbital involvement is minimal. If it were significant, one would have expected some gradation in properties down the series as the size and energy of the orbitals increased. Clearly, the nature of the cationic centre has little influence on the electronic properties of the betaines.

Table 2 ^{1}H NMR data for salts **2** (Ar = Ph, Z = OH) and betaines 7**A**; comparison of CH=N proton shifts (δ)

	Salt **2**	Betaine 7**A**
E = Sb, X = Cl	9.42	8.51
E = Sb, X = Br	9.41	8.74
E = Sb, X = Ph	9.36	8.64
E = As, X = Cl	8.70	8.12
E = As, X = Br	8.79	8.16
E = As, X = Ph	8.69	8.26



7A E = As or Sb; X = Cl, Br or Ph



7B **7C**

Experimental

^{1}H NMR spectra were recorded using a Bruker AC250 FT NMR spectrometer. Low resolution electron impact mass spectra, and related FAB MS determinations (in a *p*-nitrobenzyl alcohol matrix) were recorded using a VG Micromass 7070F instrument. High resolution accurate FAB MS determinations were recorded at the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea and Sheffield University. The UV–VIS absorption spectra were measured on a UNICAM UV$_2$-100 spectrophotometer. Solvents for spectroscopic studies were purified and dried by standard methods.

Table 3 Long-wavelength UV–VIS absorption maxima (λ_{max}/nm) of arsonium- and stibonium-iminophenolate betaine dyes 7**A** in six solvents of different polarity

	X = Cl		X = Br		X = Ph	
Solvent	E = Sb	E = As	E = Sb	E = As	E = Sb	E = As
Methanol	452	440	452	442	370	370
Acetonitrile	508	494	506	498	556	552
Acetone	538	524	534	524	590	586
Dichloromethane	536	520	534	522	578	576
THF	576	562	572	564	624	620
Ethyl acetate	570	558	566	558	620	618
Toluene	insol.	insol.	insol.	insol.	insol.	insol.

Table 4 Long-wavelength UV–VIS absorption maxima (λ_{max}/nm) of arsonium- and stibonium-iminophenol salts **2** (Ar = Ph, Z = OH) in six solvents of different polarity

	X = Cl		X = Br		X = Ph	
Solvent	E = Sb	E = As	E = Sb	E = As	E = Sb	E = As
Methanol	360	360	354	354	376	370
Acetonitrile	348	350	348	350	370	366
Acetone	350	354	352	354	370	370
Dichloromethane	358	356	354	356	380	376
THF	364	366	364	366	370	368
Ethyl acetate	354	342	348	352	370	368
Toluene	insol.	insol.	insol.	insol.	insol.	insol.

Preparation of imine intermediates

These were prepared as previously described.[2,6]

General procedure for synthesis of arsonium and stibonium salts and betaines

The appropriate *o*-bromoaryliminophenol was allowed to react with the triarylantimony or triarylarsine (1.1 mol equiv.) in acetonitrile (10 v/w of reagents) in the presence of copper(I) iodide (1 mol equiv.). The mixture was refluxed between 6 and 24 h under nitrogen for the reactions with the triarylantimony, and between 24 and 48 h for the reactions with the triarylarsine. After cooling the mixture was poured imto aqueous potassium iodide (10% w/v) and extracted three times with dichloromethane. The dried ($MgSO_4$) organic extract was reduced *in vacuo*, and the oily residue triturated several times with fresh portions of diethyl ether to give the salts.

For conversion to the related betaines, the salts were dissolved in dichloromethane, and the solution shaken with dilute aqueous sodium hydroxide solution. After drying ($MgSO_4$), the organic layer was evaporated to give the related phosphonium betaine dye. Conversion to the betaine dye was found to be unsuccessful on stirring the salt with a large excess of anhydrous potassium carbonate in acetonitrile at room temperature for 1 h.

The following compounds were characterised:

N-[(2-Triphenylarsoniobenzylidene)]-1-amino-4-methoxybenzene iodide

This was obtained as yellow crystals, mp 186 °C; $\delta_H(CDCl_3)$ 3.7 (s, 3H, OCH_3), 6.20 and 6.55 (AB, 4H, aromatic), 7.8–7.2 (m, 17H, aromatic), 8.1 (m, 1H, aromatic), 8.4 (d, 1H, aromatic), 8.7 (s, 1H, CH=N). *m*/*z* (Accurate FAB): found: 516.130334 (M^+ cation) (+1.0 ppm). $C_{32}H_{27}NAsO$ requires 516.130860 (M^+ cation). This compound was subsequently characterised by X-ray crystallography (see Discussion).

N-[(2-Triphenylstiboniobenzylidene)]-1-amino-4-methoxybenzene diiodocuprate

This was obtained as yellow crystals. Yield 77%. mp >95 °C (decomp.); $\delta_H(CDCl_3)$ 3.60 (s, 3H, OCH_3), 6.70 and 6.55 (AB, 4H, aromatic), 8.30–6.90 (m, 18H, aromatic), 8.65 (d, 1H, aromatic), 9.45 (s, 1H, CH=N). Found: Cu, 7.0%. $C_{32}H_{27}NSbO{\cdot}CuI_2$ requires Cu, 7.2%. *m*/*z* (Accurate FAB): found: 562.114831 (M^+ cation) (−3.1 ppm). $C_{32}H_{27}NSbO$ requires 562.113088 (M^+ cation).

N-[2-Tris(4-methylphenyl)stibonio]benzylidene-1-amino-4-methoxybenzene diiodocuprate

This was obtained as yellow crystals. Yield 88%. mp >110 °C (decomp.); $\delta_H(CDCl_3)$ 2.40 (s, 9H, CH_3), 3.70 (s, 3H, OCH_3), 6.75 and 6.60 (AB, 4H, aromatic), 8.20–6.90 (m, 15H, aromatic), 8.65 (d, 1H, aromatic), 9.40 (s, 1H, CH=N). Found: Cu, 6.9%. $C_{35}H_{33}NSbO{\cdot}CuI_2$ requires Cu, 6.9%. *m*/*z* (Accurate FAB): found: 604.161605 (−2.6 ppm) (M^+ cation). $C_{35}H_{33}NSbO$ requires 604.160039 (M^+ cation).

N-[(2-Triphenylstibonio)benzylidene]-4-amino-2,6-dichlorophenol diiodocuprate

This was obtained as a pale orange solid (80%), mp *ca.* 121–124 °C. $\delta_H(CDCl_3)$ 6.5 (s, 2H, aromatic), 7.23–7.70 (m, 17H, aromatic), 8.00 (t, 1H, aromatic), 8.71(d, 1H, aromatic), 9.41 (s,1H, CH=N). *m*/*z* (Accurate FAB): found: 616.020261 (M^+ cation) (−1.2 ppm). $C_{31}H_{23}SbNCl_2O$ requires 616.019494 (M^+ cation).

N-[(2-Triphenylstibonio)benzylidene]-4-amino-2,6-dichlorophenolate

This was obtained as a dark orange–red solid (94%), phase change 210 °C, mp 215 °C. $\delta_H(CDCl_3)$ 6.5 (s, 2H), 7.09 (d, 1H), 7.43–7.58 (m, 16H), 7.81 (d, 1H), 7.94 (d, 1H), 8.51 (s, 1H, CH = N). *m*/*z* (Accurate FAB): found: 616.019614 (M + 1, cation) (−0.2 ppm). $C_{31}H_{23}NSbCl_2O$ requires 616.019494 (M + 1, cation).

N-[(2-Triphenylstibonio)benzylidene]-4-amino-2,6-dibromophenol diiodocuprate

This was obtained as a pale orange solid (70%), mp *ca.* 121–124 °C. $\delta_H(CDCl_3)$ 6.72 (s, 2H), 7.26–7.75 (m, 17H), 8.02 (t, 1H), 8.70 (d, 1H), 9.41 (s, 1H, CH=N). *m*/*z* (Accurate FAB): found 703.918504 (M^+, cation) (−0.1 ppm). $C_{31}H_{23}NSbBr_2O$ requires 703.918460 (M^+, cation).

N-[(2-Triphenylstibonio)benzylidene]-4-amino-2,6-dibromophenolate

This was obtained as a dark red solid (96%), phase change 165 °C, mp 177–178 °C. $\delta_H(CDCl_3)$ 6.76 (s, 2H), 7.11–7.14 (d, 1H), 7.26–7.67 (m, 16H), 7.76–7.82 (t, 1H), 7.93–7.96 (d, 1H) 8.74 (s, 1H, CH=N). *m*/*z* (Accurate FAB): found: 703.920763 (M + 1, cation) (−3.3 ppm) $C_{31}H_{23}NSbBr_2O$ requires 703.918460 (M + 1, cation).

N-[(2-Triphenylstibonio)benzylidene]-4-amino-2,6-diphenylphenol diiodocuprate

This was obtained as a pale yellow solid (67%), mp 128–129 °C. $\delta_H(CDCl_3)$ 6.56 (s, 2H, aromatic), 7.23–7.72 (m, 26H, aromatic), 8.03–8.09 (t, 2H, aromatic) 8.59 (d, 1H, aromatic), 9.36 (s, 1H, CH=N). *m*/*z* (Accurate FAB): found: 700.160044 (M^+ cation) (0.00 ppm). $C_{43}H_{33}NSbO$ requires 700.160039 (M^+cation).

N-[(2-Triphenylstibonio)benzylidene]-4-amino-2,6-diphenylphenolate

This was obtained as a dark purple solid (91%), phase change 83 °C, mp *ca.* 110 °C. $\delta_H(CDCl_3)$ 6.22 (s, 2H, aromatic), 6.39–8.07 (m, 29H, aromatic), 8.64 (s, 1H, CH=N). *m*/*z* (Accurate

FAB): found: 700.165527 (M + 1, cation) (−7.8 ppm) $C_{43}H_{33}NSbO$ requires: 700.160039 (M + 1, cation).

N-[(2-Triphenylarsonio)benzylidene]-4-amino-2,6-dichlorophenol diiodocuprate

This was obtained as a pale orange solid (48%), mp 128–130 °C. $\delta_H(CDCl_3)$ 6.13 (s, 2H, aromatic), 7.27–7.71 (m, 16H, aromatic), 7.81 (t, 2H, aromatic), 8.52 (d, 1H, aromatic), 8.70 (s, 1H, CH=N). Found: Cu 8.7. $C_{31}H_{23}NAsCl_2O{\cdot}CuI_2$ requires Cu 8.0%. *m*/*z* (Accurate FAB): found: 570.038449 (M^+ cation) (−2.1 ppm). $C_{31}H_{23}NAsCl_2O$ requires 570.037266 (M^+ cation).

N-[(2 -Triphenylarsonio)benzylidene]-4-amino-2,6-dichlorophenolate

This was obtained as a red solid (97%), phase change 115 °C, mp 125 °C. $\delta_H(CDCl_3)$ 6.15 (s, 2H, aromatic), 7.27–7.86 (m, 19H, aromatic), 8.12 (s, 1H, CH=N). *m*/*z* (Accurate FAB): found: 570.039011 (M + 1, cation) (−3.1 ppm). $C_{31}H_{23}NAsCl_2O$ requires 570.037266 (M + 1, cation).

N-[(2 -Triphenylarsonio)benzylidene]-4-amino-2,6-dibromophenol diiodocuprate

This was obtained as a pale orange solid (53%), mp 127–130 °C. $\delta_H(CDCl_3)$ 6.31 (s, 2H, aromatic), 7.26–7.80 (m, 16H, aromatic), 8.09 (t, 2H, aromatic), 8.51 (d, 1H, aromatic), 8.79 (s, 1H, CH=N). *m*/*z* (Accurate FAB): found: 657.936556 (M^+ cation) (−0.5 ppm). $C_{31}H_{23}NAsBr_2O$ requires 657.936232 (M^+ cation).

N-[(2-Triphenylarsonio)benzylidene]-4-amino-2,6-dibromophenolate

This was obtained as a red solid (90%), decomp. >150 °C. $\delta_H(CDCl_3)$ 6.39 (s, 2H, aromatic), 7.12–7.90 (m, 19H, aromatic), 8.16 (s, 1H, CH=N). *m*/*z* (Accurate FAB): found 657.937760 (M + 1, cation) (−2.3 ppm). $C_{31}H_{23}NAsBr_2O$ requires 657.936232 (M + 1, cation).

N-[(2-Triphenylarsonio)benzylidene]-4-amino-2,6-diphenylphenol diiodocuprate

This was obtained as a beige–yellow solid (37%), phase change 110 °C, mp 127 °C. $\delta_H(CDCl_3)$ 6.11 (s, 2H, aromatic), 7.26–7.77 (m, 26H, aromatic), 8.10 (t, 2H, aromatic), 8.35 (d, 1H, aromatic), 8.69 (s, 1H, CH=N). Found: Cu, 5.6. $C_{43}H_{33}NAsO{\cdot}CuI_2$ requires Cu, 6.5%. *m*/*z* (Accurate FAB): found: 654.178826 (M^+ cation) (−1.6 ppm). $C_{43}H_{33}NAsO$ requires 654.177810 (M^+ cation).

N-[(2-Triphenylarsonio)benzylidene]-4-amino-2,6-diphenylphenolate

This was obtained as a dark purple solid (89%), phase change 125 °C, mp 150–152 °C. $\delta_H(CDCl_3)$ 6.35 (s, 2H, aromatic), 7.06–7.83 (m, 29H, aromatic), 8.26 (s, 1H, CH=N). *m*/*z* (Accurate FAB): found: 654.173591 (M + 1, cation) (6.4 ppm). $C_{43}H_{33}NAsO$ requires 654.177810 (M + 1, cation).

2-{2-[Tris(4-methylphenyl)stibonio]phenyl}benzothiazole diiodocuprate

This was obtained as a beige solid. Yield 86%, mp >105 °C (decomp.). $\delta_H(CDCl_3)$ 2.4 (s, 9H, CH_3), 8.50–6.70 (m, 20H, aromatic). Found: Cu, 6.4. $C_{34}H_{29}NSSb{\cdot}CuI_2$ requires Cu, 6.98%. *m*/*z* (Accurate FAB): found: 604.107879 (−3.3 ppm) (M^+ cation). $C_{34}H_{29}NSSb$ requires: 604.105896 (M^+ cation).

2-[2-(Triphenylstibonio)phenyl]benzothiazole diiodocuprate

This was obtained as a beige solid, Yield 100%. mp 138–140 °C. Found: Cu, 7.8. $C_{31}H_{23}NSSb{\cdot}CuI_2$ requires Cu, 7.32%. *m*/*z* (accurate FAB): found 562.060441 (M^+ cation) (−2.7 ppm). $C_{31}H_{23}NSSb$ requires 562.058945 (M^+ cation).

X-Ray crystallography for *N*-[(2-Triphenylarsoniobenzylidene)]-1-amino-4-methoxybenzene iodide

Crystal data. Empirical formula $C_{32}H_{27}AsINO$, $M = 643.37$, orthorhombic, space group $P2_12_12_1$, $a = 10.337(2)$, $b = 15.2970(13)$, $c = 17.3890(6)$ Å, $V = 2749.6(5)$ Å^3, $Z = 4$, reflections collected 10794, 4165 unique ($R_{\mathrm{int}} = 0.088$), final $wR_2 = 0.0766$ (all data), $R = 0.0326$ [$I > 2\sigma(I)$], $\lambda = 0.71069$ Å, μ(Mo-Kα) = 23.84 cm^{-1}, $T = 150$ K.

Intensity data were collected on a FAST area detector diffractometer in a manner described previously.[17] The structure was solved *via* direct methods (SHELXS-96)[18] and refined on F^2 by full-matrix least squares using all unique data (SHELXL-93).[19] All non-hydrogen atoms were anisotropic, and hydrogen atoms were included in calculated positions (riding model). The final value of the Flack parameter [−0.04(2)] indicated the determination of the correct absolute structure. Full details of structure determination and crystallographic results have been deposited with Cambridge Crystallographic Data Centre, CCDC 1145/198.

See http://www.rsc.org/suppdata/jm/a9/a907699i/ for crystallographic files in .cif format.

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Paper a907699i