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Characterising secondary bonding interactions within triaryl organoantimony(V) and organobismuth(V) complexes

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The thermodynamically preferred conformations of the five-co-ordinate trigonal-bipyramidal complexes $SbPh_3Cl_2$ **1** and $BiPh_3Cl_2$ **2**, determined *via* van der Waals energy calculations, have been found to be in good agreement with the corresponding correlated propeller arrangements which are observed in the solid state. However, similar calculations upon the corresponding diesters $SbPh_3(O_2CR)_2$ **3** and $BiPh_3(O_2CR)_2$ **4** [R = $C(OH)Ph_2$ **a** or C_6H_4OH-*o* **b**] were at variance with the solid state, thereby indicating the participation of stabilising secondary bonding interactions between the metal centre and the carbonyl oxygen atom of the ester moiety. In accord with current Lewis acid–base bonding models, a strong correlation was found to exist between the pK_a of the parent acid and the magnitude of the M···O=C interaction. The complexes **3a**,**3b** and **4a**,**4b** were prepared in order to probe the effect of strong intramolecular hydrogen bonding upon the ability of ester ligands to stabilise sterically disfavoured conformations *via* σ_{nb} donation. Single crystal X-ray analyses of **3a**,**3b** and **4a** demonstrate that although significant attenuation of the M···O=C interaction is achieved *via* strong intramolecular hydrogen bonding, sterically disfavoured arrangements predominate in the solid state.

The preferred geometry of five-co-ordinate Group 15 elements[1] is the trigonal bipyramid (*TBPY*), which is generally accepted to be a fluxional, stereochemically non-rigid or pseudo-rotating[2] arrangement rapidly interconverting with the square-pyramidal (*SP*) structure. A delicate balance exists between the two structural forms, both in solution[3] and the solid state where intermolecular packing interactions[4] are believed to play a determining role. For example, the solid state structures of $AsPh_5$ and the corresponding cyclohexane solvates $AsPh_5\cdot 0.5C_6H_{12}$ and $SbPh_5\cdot 0.5C_6H_{12}$ adopt a *TBPY* geometry, whereas $SbPh_5$ and $BiPh_5$ adopt an *SP* arrangement.[5] The well established[6] Lewis acidity of antimony(III) and bismuth(III) species affords structurally diverse[7] addition compounds in the solid state *via* secondary bonding interactions. Here, a bonding model which invokes donation into Sb–L/Bi–L σ* acceptor orbitals has been proposed in order to rationalise the expansion and distortion of the co-ordination sphere about the metal centre in these and related complexes.[8] The co-ordination sphere of antimony(V) complexes undergoes a well characterised expansion and distortion in order to form solid-state addition complexes. The formation of such Lewis acid–base complexes is generally accommodated *via* the *SP* geometry, which presents a vacant axial co-ordination site for secondary bonding.[9] Complexes in which donor ligands are constrained close to or within the primary co-ordination sphere have been shown to undergo intra-molecular chelation.[10] The metal co-ordination sphere of *TBPY* antimony- and bismuth-(V) complexes, possessing axial carboxylic ester ligands, may be considered seven-co-ordinate, as the primary M–O bonding interaction is augmented by weaker secondary M···O=C interactions. In the case of suitably substituted complexes such as $SbPh_3(O_2CC_5H_4N$-*o*$)_2$ one of the secondary M···O=C bonds may be usurped by an M···N interaction.[11] We present here a study of *TBPY* complexes of Sb^V and Bi^V in the solid state in order to characterise both the conformations and secondary bonding interactions exhibited by axial carboxylic ester ligands. In addition, the study provides an opportunity to correlate in a qualitative fashion distortions of the metal co-ordination sphere with a bonding model currently used to rationalise the Lewis acidity of complexes of Sb and Bi.[8] Finally, the conformational analysis of *TBPY* complexes possessing equatorially displaced aryl ligands provides a contribution towards understanding the stereochemical outcome of nucleophilic substitution reactions at tetrahedral phosphorus.[12]

Results and discussion

It is well known that both triphenylantimony and triphenylbismuth dichlorides (**1** and **2**, Scheme 1) undergo metathetical reactions with the silver salts of carboxylic acids to afford biscarboxy esters of the form $MPh_3(O_2CR)_2$.[13] Organo-antimony and -bismuth complexes of the type **3**,**4**, derived from benzilic and salicylic acids (**a** and **b**, respectively: Scheme 1) were prepared by stirring a THF solution of **1** or **2** with a twofold excess of the silver salts of **a**,**b** overnight under nitrogen. The complexes **3a**,**3b** and **4a**,**4b** were fully characterised *via* $^1H/^{13}C$ NMR, IR, and elemental analysis.

The preferred arrangement of a triaryl system is governed by a balance between inter ring–ring and inter ring–ligand steric interactions.[14] The phenyl rings in PPh_3, for example, minimise intramolecular interactions by allowing the P–C_i bonds to twist in the same sense, thereby affording a correlated arrangement.[15] Such correlated[16] triaryl systems contain an axis of helical chirality which can be described in terms of two enantiomeric propeller configurations; *i.e.* clockwise (*P*) and anticlockwise (*M*).[17] It is reasonable to anticipate that the phenyl rings co-ordinated to the equatorial sites of a *TBPY* complex such as **1** or **2** (Scheme 1) may also minimise inter ring–ring and inter ring–ligand interactions by adopting a correlated arrangement. Newman projections (viewed along the Cl–M bond) of the

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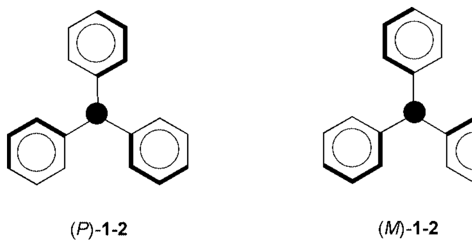
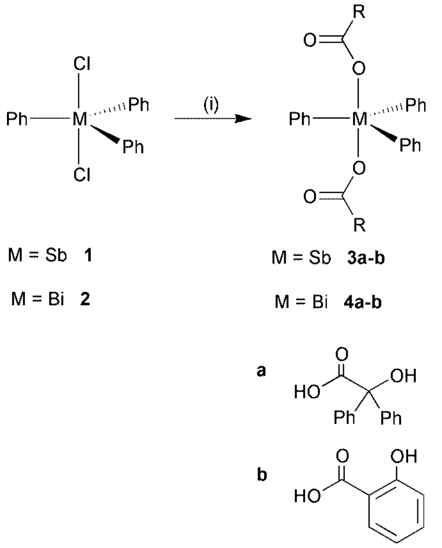


Fig. 1 Newman projections (viewed along the Cl–M bond) of the preferred degenerate conformations of complexes **1** and **2**.



Scheme 1 Reagents: (*i*) silver salt of **a**,**b**, THF, rt, 12 h.

predicted lowest energy arrangements *P* and *M* for complexes **1** and **2** are presented in Fig. 1. A brief analysis of the preferred arrangements of the triaryl moiety within *TBPY* complexes such as **1** and **2** (which contain spherically symmetrical apical ligands) is presented in advance of a discussion related to relatively complicated systems such as **3** and **4**.

Computer models[†] using van der Waals interaction energy calculations assume that the thermodynamically preferred arrangement of a molecular system is governed by intramolecular steric interactions. This approach has proved remarkably successful in predicting the conformations of a variety of organometallic fragments in which stereoelectronic contributions to complex stability may be ignored.[18] The thermodynamically preferred conformation of the triaryl propeller moiety in **1**,**2** was determined in the following manner. A generic model of the complex MPh_3Cl_2 was constructed using average bond lengths and angles derived from previously reported solutions to the structures of $SbPh_3Cl_2$ and $BiPh_3Cl_2$.[19] The torsion angles ω[‡] were set to 0°, thereby affording a D_{3h} symmetrical starting structure for the calculations. The torsion angle ω for the C_2 symmetric phenyl rings were driven independently through the range 0–180° in 10° increments. At each point the total van der Waals interaction energy was allowed to minimise by independent rotation about all $M–C_i$ bonds until the default energy convergence criteria were achieved. Selected crystallographic data for all solutions to the structures **1** and **2** are presented in Table 1. As expected, the calculated lowest energy conformation ($\omega_{A–C}$ = *ca.* −65°) is correlated and corresponds reasonably well with the structures observed in the solid state. Calculations and crystallographic correlations upon pyramidal propeller systems such as PPh_3 indicate that a range of values of ω ($\Delta\omega$ *ca.* ±10°) are energetically tolerable.[15] The average value of ω_{calc} (−65°) > ω_{cryst} (−45°), which may indicate that the calculation underestimates the steric pressure exerted by the axial Cl ligands upon the *ortho* C/H atoms of the phenyl rings in the solid state. Furthermore, the rigid-model approach is unable to mimic the phenomena of ligand tilting, which has been shown to accompany pronounced inter ring–ligand interactions ($\omega \rightarrow 0°$).[16]

Table 1 Crystallographic correlations for complexes of the type MPh_3Cl_2 **1**,**2**

Complex	Metal	ω_A/°	ω_B/°	ω_C/°
Calculated	—	−67	−66	−64
BUMGEV[19a]	Sb	−33	−47	−76
PCSTIB[19b]	Sb	−49	−43	−44
TOYMUP[19c]	Sb	−68	−48	−29
PCSTIB2[19d]	Sb	−59	−28	−48
PCSTIB1[19e]	Sb	+6	−32	−61
		−20	−38	−57
BITPHC10[19f]	Bi	−17	−25	−58

Having established the preferred arrangement of three phenyl rings co-ordinated to the equatorial sites of a *TBPY* (*i.e.* **1**,**2**), attention turns to the perturbation accompanying the replacement of the apical Cl atoms with carboxylic ester ligands (*i.e.* **3**,**4**). Newman projections (viewed along the O–M bond) of *trans* and *cis* diesters, superimposed upon the correlated conformation of an MPh_3 moiety within a *TBPY* arrangement **I**, are presented in Fig. 2. The closed circle represents the C=**O** atom of the carboxy-ester above the plane of the equatorial ligands. Conversely, the open circle represents the C=**O** atom of the carboxy-ester below the plane of the equatorial ligands. Upon inspection, it is clear that both correlated arrangements incur destabilising inter ring–ligand interactions. In *trans*-**I** both edges (C_o/H_o) of ring **B** experience destabilising interactions with the ester ligands above and below the equatorial plane. Ring **B** may alleviate inter ring–ligand interactions by undergoing C_i–M bond rotation, thereby affording the decorrelated arrangement *trans*-**II** (Fig. 2). In *cis*-**I** the edges of rings **B** and **C** also experience destabilising steric interactions with the ester ligands above and below the equatorial plane, respectively. These interactions may be alleviated by C_i–M bond rotations, which decorrelate the propeller system and orient the planes of rings **B** and **C** approximately orthogonal to the M–O bond. Ring **A** will tend towards a coplanar arrangement with respect to the O–M–O bond axis in order to relieve the inter ring–ring steric pressure which attends the reorientation of rings **B**/**C**. Therefore, the arrangement predicted for *cis* disposed esters is the decorrelated *cis*-**II** (Fig. 2) conformation. One immediately notes that the *cis*-**II** arrangement orients both σ_{nb} donating C=**O** groups of the ester ligands approximately *anti* to the $M–C_{ipso}$ bond of ring **A**, thereby affording a propitious geometrical arrangement for $M–Ph_A\ \sigma^* \longleftarrow \sigma_{nb}$ orbital overlap.[8] On steric grounds alone, however, it is anticipated that the energy content of decorrelated *cis*-**II** will be greater than that of decorrelated *trans*-**II**, as the former is accompanied by inter (ring **A**–ligand) and (ring **C**–ring **B**) interactions which are absent in the latter.

The thermodynamically preferred conformation of a generic complex of type **3** or **4** was calculated in a manner similar to that described earlier for **1** and **2**. The crystal structure of

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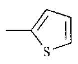
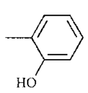
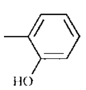
[†] Molecular modelling calculations were carried out using the Chem-X package, distributed by Chemical Design Ltd., Oxford Molecular Group, The Medawar Centre, Oxford Science Park, Oxford, UK OX4 4GA.

[‡] The torsion angle ω is defined by $C_{ortho}–C_{ipso}–M–Cl$. A negative value corresponds to a clockwise torsion and therefore clockwise (*P*) helical chirality. A positive value denotes an anticlockwise torsion and an anticlockwise (*M*) sense of helical chirality. In this study we discuss the conformations of triaryl moieties within achiral metal complexes. Consequently, we arbitrarily choose to consider the clockwise (*i.e.* $-\omega$) helical configuration. The argument put forward for the clockwise configuration applies equally to the degenerate enantiomeric anticlockwise case.

Table 2 Crystallographic correlations for complexes of the type $SbPh_3(O_2CR)_2$ **3**

Class	Complex	R	$Sb\cdots O^{a}$/Å	θ^{b}/°	pK_a[22]
cis-**II**	NAGXOI[21a]	CH=CHPh	2.66	151	4.44
	BOYFIE[21b]	Ph	2.75	150	4.19
	TPSBDA[21c]	CH_3	2.78	148	4.75
	SEBCOR[21d]		2.84	146	3.50
	3a	$C(OH)Ph_2$	2.99	138	3.05
	3b		3.15	129	2.83
trans-**II**	**3b**		3.17	—	2.83
	PABJIL[20c]	CF_3	3.22	—	0.52

[a] Average Sb · · · O distance. [b] $\theta = C_i(\mathbf{B})–Sb–C_i(\mathbf{C})$. Unless stated otherwise $C_i–Sb–C_i \approx 120°$.

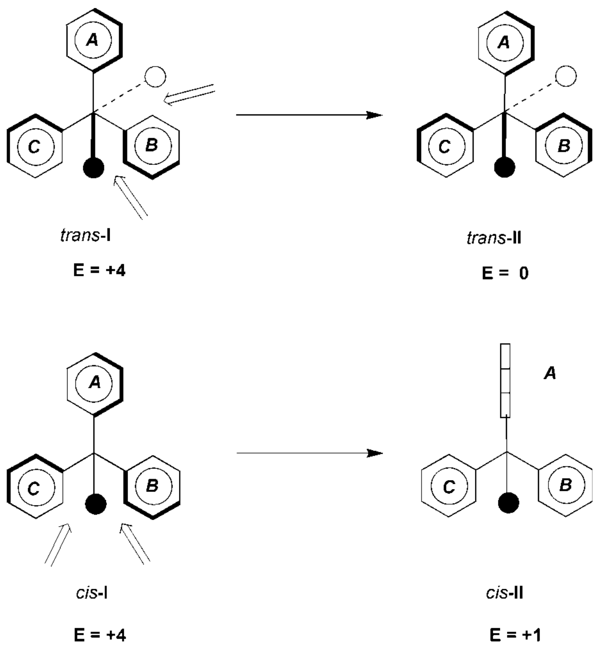


Fig. 2 The predicted destabilisation of a correlated MPh_3 moiety (**I** ⟶ **II**) by diaxial *trans* and *cis* esters in a *TBPY* complex. ΔE for the conformers *cis*/*trans*-(**I**,**II**) are calculated with respect to the global minimum ($E = 0$), and represent a ratio of energy differences.

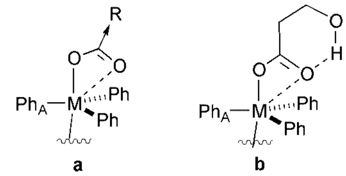


Fig. 3 Asymmetric bidendate bonding modes destabilised by (**a**) electron withdrawing substituents and (**b**) intramolecular hydrogen bonding.

$BiPh_3(O_2CH)_2$ (LAVNUR,§ Table 3[20]) provided an excellent starting point for our calculations. Bond lengths and angles were regularised to ensure an idealised *TBPY* arrangement. All three phenyl rings were driven about $\omega = 0–180°$ in 10° increments, and both M–O bonds were driven 0–360° in 10° increments. At each increment the total van der Waals interaction energy content was allowed to minimise by independent rotations about all M–C and M–O bonds, until the default energy convergence criteria were achieved. As expected, the calculated lowest energy arrangement ($\omega_A = +66°$, $\omega_B = -80°$, $\omega_C = +63°$) was found to be in excellent agreement with *trans*-**II** (Fig. 2), which has been designated to be of zero energy ($E = 0$) relative to all other conformations which shall be discussed here. Single point energy calculations upon the correlated arrangements *trans*-**I** and *cis*-**I** were performed using calculated values of $\omega_{A–C} = -65°$ derived from complexes **1** and **2**. As expected, the energy contents of *trans*- and *cis*-**I** were found to be identical (as both arrangements incur the same number and type of inter ring–ring and ring–ligand interactions) and greater than that found for *trans*-**II**. The van der Waals energy of *cis*-**I** was allowed to minimise *via* independent M–C_i bond rotations. The resulting arrangement ($\omega_A = +60°$, $\omega_B = +88°$, $\omega_C = +88°$), which is found to be in good agreement with that predicted (*i.e.* *cis*-**II**), is lower in energy than that of *cis*/*trans*-**I**, but higher in energy than that of *trans*-**II**. The ratio of the calculated energy differences (ΔE) for *cis*/*trans*-**I** and *cis*-**II** with respect to the global minimum ($E = 0$; *trans*-**I**) indicate that the intramolecular steric strain decreases in the order *cis*/*trans*-**I** ≫ *cis*-**II** > *trans*-**I** (Fig. 2).

Selected crystallographic data for all reported complexes of the type $MPh_3(O_2CR)_2$ (M = Sb or Bi) are presented in Tables 2[21] and 3,[20] respectively. Using the classifications outlined earlier, the complexes have been arranged according to the type of conformation adopted in the solid state. As expected, the relatively sterically strained arrangements of type **I** are not observed in the solid state. Surprisingly however, only one example consistent with the thermodynamically preferred *trans*-**II** arrangement (M = Sb, R = CF_3)[20c] has been observed in the solid state. All other previously reported complexes adopt the *cis*-**II** arrangement. The antimony complexes in Table 2 have been arranged in order of increasing Sb · · · O=C distance. It can be seen that for *cis*-**II** arrangements the C_i–Sb–C_i (θ) angle for rings **B**,**C** increases with decreasing Sb · · · O=C distance, presumably in order to accommodate the accompanying steric infringement by the axial ligands. A reasonable correlation also exists between the pK_a[22] of the parent acid and the observed Sb · · · O=C distance; the weaker the parent acid, the shorter is the Sb · · · O=C distance. This observation is consistent with asymmetric bidentate bonding by the metallic ester moiety (Fig. 3a). Although caution must be exercised when making correlations between solution and solid state data, it is reasonable to suggest that strongly electron withdrawing substituents upon the carboxy moiety (*i.e.* R = CF_3, PABJIL[20c]) attenuate the asymmetric Sb · · · O=C bidentate interaction to such an extent that the *cis*-**II** conformer is destabilised with respect to the *trans*-**II**.

All previously reported bismuth complexes of type **4** adopt the *cis*-**II** arrangement in the solid state (Table 3). In general,

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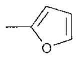
§ Cambridge Structural Database refcode.

Table 3 Crystallographic correlations for complexes of the type $BiPh_3(O_2CR)_2$ **4**

Class	Complex	R	Bi···O[a]/Å	θ[b]/°	pK_a[22]
cis-**II**	NAXVEN[13b]	$(CH_2)_3OH$	2.79	150	4.72
	NAXWEO[13b]	$CH(Ph)CH_2OH$	2.80	150	4.30
	GEMGOU[20a]		2.80	148	3.25
	NAXVIR[c,13b]	$(CH_2)_2C_6H_4OH$-*p*	2.88	146	—
	LAVNUR[20b]	H	2.91	145	3.70
	PABJEH[20c]	CF_3	2.98	140	0.52
	3a	$C(OH)Ph_2$	2.99	138	3.05

[a] Average Bi···O distance. [b] θ = C_i(**B**)–Bi–C_i(**C**). [c] Orientation of rings **A**–**C** distorted by interference with axial ligands.

the correlation between M···O=C and pK_a is as noted in the case of Sb. A most instructive anomaly exists in the case of the diester of CF_3CO_2H (PABJEH[20c]), which despite possessing a weak M···O=C (2.98 Å) interaction adopts the *cis*-**II** and not the *trans*-**II** conformer as observed for the corresponding antimony complex (Sb···O=C 3.22 Å). This is consistent with the conjugative bonding model which suggests that Bi possesses a lower energy σ^* orbital than does Sb, thereby promoting a greater degree of $\sigma_{nb} \longrightarrow \sigma^*$ orbital overlap in the former.[8] Further attenuation of the Bi···O=C interaction, and destabilisation of the *cis*-**II** conformer, may be achieved by replacing the phenyl rings in $BiPh_3(O_2CCF_3)_2$ with aromatic ligands capable of dispersing greater electron density onto the Bi (*i.e.* *p*-$R_2NC_6H_4$). Depolarising the Bi–C bonds in this manner raises the energy of the σ^* orbital thereby reducing the extent of $\sigma_{nb} \longrightarrow \sigma^*$ orbital overlap. A significant weakening of the Bi···O=C interaction (3.16 Å) is indeed observed in the complex Bi(*p*-$R_2NC_6H_4)_3(O_2CCF_3)_2$ (REPYUG),[23] however the solid-state preference for the *cis*-**II** arrangement remains. Similarly, X-ray crystallography demonstrates that the diesters $MPh_3(SO_3Ph)_2$ (M = Sb[24] or Bi[24]) derived from benzenesulfonic acid (pK_a = 2.55) exhibit the same preference; namely Sb adopts the *trans*-**II** and Bi adopts the *cis*-**II** arrangement. Although the average Bi···O=C distances (3.28 Å) are particularly long, the sterically disfavoured *cis*-**II** arrangement is still preferred, which may indicate particularly favourable $\sigma_{nb} \longrightarrow \sigma^*$ orbital overlap.[25]

Further study into the contrasting conformations adopted by a given ligand, and the propensity of bismuth diesters to adopt the *cis*-**II** arrangement, required an analysis of complexes of types **3**,**4a**,**4b**. The ability of α- and β-hydroxy substituents to increase the acidity of carboxylic acids is well known. The difference in acidity between 4- and 2-hydroxybenzoic acids (ΔpK_a = 1.65) is generally explained on the basis of intramolecular hydrogen bonding.[26] Thus, aliphatic α-hydroxy (benzilic acid **a**, Scheme 1) and aromatic β-hydroxy (2-hydroxybenzoic acid **b**, Scheme 1) carboxylic acids were chosen for their attenuated donor properties. In this way it was envisaged that Bi···O=C interactions in particular would be weakened (Fig. 3, **b**), thereby destabilising the *cis*-**II** conformer with respect to the *trans*-**II**. Crystal structure data were obtained for the diester complexes derived from benzilic acid **3a**,**3b** and 2-hydroxybenzoic acid **4a**. Unfortunately, it was not possible to grow single crystals of **4b** suitable for X-ray crystallography.

Selected bond lengths and angles for the crystal structures of **3a**,**3b** and **4a** are presented in Table 4. The structure of $SbPh_3[O_2CC(OH)Ph_2]_2$ **3a**, shown in Fig. 4, exhibits a slightly distorted *TBPY* geometry where the axial substituents adopt values close to ideal, whilst the equatorial angles deviate from those expected as a result of the orientations adopted by the tilted phenyl rings. The geometry of the remainder of the molecule primarily arises from a combination of steric demands and non-bonded interactions. A number of strong intramolecular interactions constrain the conformation adopted by the ester moieties with respect to the phenyl rings [C14···O1 2.887(3), C18···O4 2.886(3), C42···O4 3.180(3) and C46···O6 2.802(4) Å]. Several different intermolecular interactions are also present, such as X–H···π with phenyl rings, close contacts and hydrogen bonds, the most significant of these being O3···O6 3.252(3), O6···O2 2.819(3) Å, which form an infinite network.

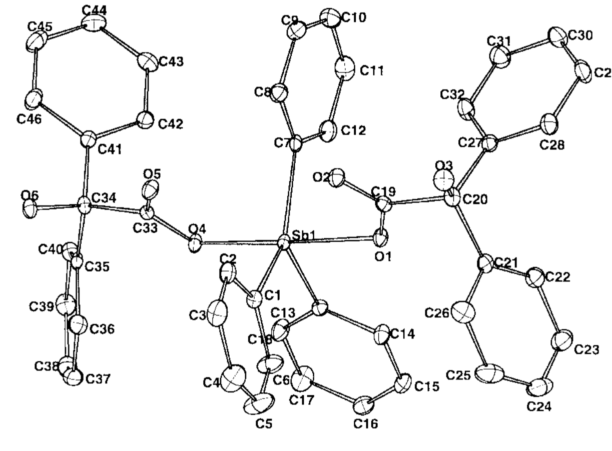


Fig. 4 The molecular structure of $SbPh_3[O_2CC(OH)Ph_2]_2$ **3a**, with 50% probability thermal ellipsoids.

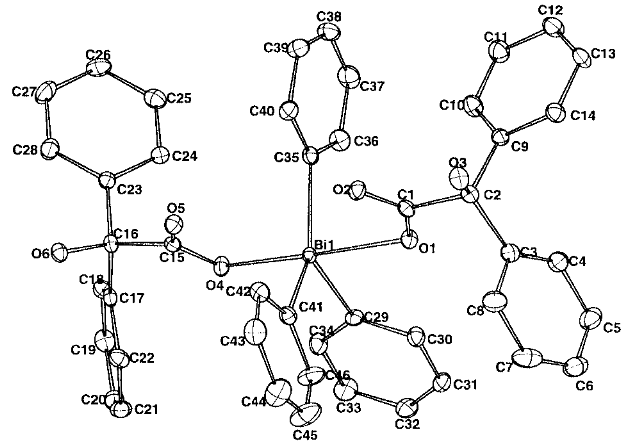


Fig. 5 The molecular structure of $BiPh_3[O_2CC(OH)Ph_2]_2$ **4a**, with 50% probability thermal ellipsoids.

The structure of $BiPh_3[O_2CC(OH)Ph_2]_2$ **4a** is shown in Fig. 5 and is seen to be isostructural with $SbPh_3[O_2CC(OH)Ph_2]_2$ **3a**, upon comparison of lattice parameters and atomic coordinates. Therefore the structural features of the bismuth analogue are virtually identical with those of $SbPh_3[O_2CC(OH)Ph_2]_2$ and the structural discussion above also applies to **4a**. Although intramolecular hydrogen bonding succeeds in attenuating the M···O=C interaction (2.99 Å),[27] both complexes adopt the sterically disfavoured *cis*-**II** arrangement. For the antimony

Table 4 Selected equivalent bond lengths (Å) and angles (°) for $SbPh_3[O_2CC(OH)Ph_2]_2$ **3a**, $SbPh_3[O_2CC_6H_4OH\text{-}o]_2$ **3b** and $BiPh_3[O_2CC(OH)Ph_2]_2$ **4a**

	3a	**4a**	**3b** (*cis*-**II**)	**3b** (*trans*-**II**)
M–O_{ax}	2.102(2)	2.292(2)	2.127(3)	2.107(3)
	2.145(2)	2.249(2)	2.100(3)	2.102(3)
M–C_{eq}	2.100(3)	2.194(3)	2.097(4)	2.096(4)
	2.109(2)	2.193(3)	2.095(4)	2.099(4)
	2.109(2)	2.210(2)	2.100(4)	2.097(4)
O–M–O	171.98(7)	167.34(7)	168.05(11)	177.44(11)
O_a–M–C	97.66(9)	90.60(9)	90.43(13)	89.20(13)
	89.58(8)	85.50(8)	93.10(13)	85.53(13)
	87.77(9)	85.63(8)	82.86(13)	94.93(14)
O_b–M–C	89.93(9)	100.77(9)	94.59(13)	93.36(13)
	86.37(8)	89.35(9)	92.09(13)	92.85(13)
	87.64(8)	86.22(9)	85.19(14)	83.90(14)
C–M–C	138.70(10)	138.57(10)	129.28(15)	125.37(15)
	106.19(10)	104.93(10)	114.14(16)	120.47(16)
	114.71(10)	115.83(10)	116.51(16)	114.15(16)

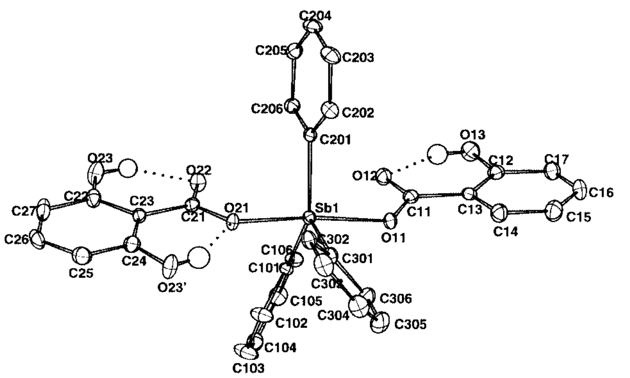


Fig. 6 Molecule **A** of $SbPh_3[O_2CC_6H_4OH\text{-}o]_2$ **3b** in the *cis*-**II** form.

complex **3a** the longest M···O=C distance is observed for such an arrangement. The pK_a of benzilic acid correlates well with M···O=C distances observed in the solid state (Tables 2 and 3).

The complex $SbPh_3[O_2C_6H_4OH\text{-}o]_2$ **3b** (Figs. 6 and 7) crystallises with two independent molecules in the asymmetric unit, in addition to a total of one trichloromethane arising from two partially occupied and disordered molecules (75 and 25%). Moreover, the two independent molecules are in fact the *cis*-**II** and *trans*-**II** conformers, which co-crystallise in the same unit cell. The strong hydrogen-bond donating ability of the 2-hydroxy moiety within the salicylic ester ligand significantly weakens the Sb···O=C interaction in **3b** compared to **3a**, thus permitting the crystallisation of both isomers. Inspection of bond lengths and angles shows no significant difference in the metal co-ordination geometry between the two conformers and a comparable degree of distortion to that observed in **3a**.

Disorder in one salicylic ester moiety of the *cis*-**II** conformer results in two orientations of the phenolic group being present with 75 and 25% partial occupation, respectively. These are uniquely fixed *via* strong hydrogen bonds from the hydroxy group to both the carbonyl [O23–H23···O22 2.593(5) Å] and ether [O23′–H23′···O21 2.541(13) Å] oxygen atoms. The second salicylic ester ligand of this structure and indeed the *trans*-**II** conformer also exhibit the same hydroxyl–carbonyl interaction [O13–H13···O12 2.625(6), O33–H33···O32 2.607(6) and O43–H43···O42 2.608(5) Å respectively]. Investigation of the supramolecular assembly formed shows O13 to be a bifurcated hydrogen bond donor, as in addition to the intramolecular interactions it is the only intermolecular hydrogen-bond donor present in the structure [O13–H13···O43 3.047(4) Å].

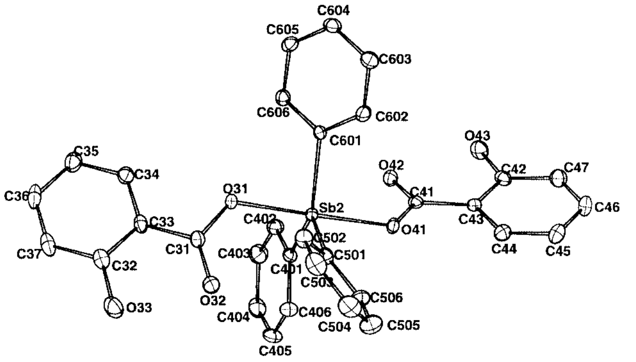


Fig. 7 Molecule **B** of $SbPh_3[O_2CC_6H_4OH\text{-}o]_2$ **3b** in the *trans*-**II** form.

In conclusion, studies in the solid state indicate that sterically disfavoured conformations of *TBPY* antimony(V) and bismuth(V) complexes may be stabilised by secondary bonding interactions involving diaxially co-ordinated ester ligands. The complex geometries accompanying the expansion of the co-ordination sphere from five to seven is consistent with current bonding models which invoke hyperconjugative $\sigma^* \longleftarrow \sigma_{nb}$ bonding interactions. Thus, a weakening of the M···O=C secondary interaction is facilitated by (a) attenuating the σ_{nb} donating ability of the axial ligand, or (b) diminishing the M–C bond polarity. As anticipated by the model, the Lewis acidity of Bi is found to be greater than that of Sb. Crystallographic evidence suggests that the propensity to stabilise certain conformations *via* secondary bonding interactions extends to the analogous compounds of Sn. Further reports upon the implications of these phenomena will follow in due course.

Experimental

General

All reactions were performed under an atmosphere of dry nitrogen. Tetrahydrofuran (THF) was distilled under an atmosphere of nitrogen from sodium–benzophenone. Unless otherwise stated, all other materials were purchased from Aldrich and used without further purification. Silver salts of carboxylic acids were prepared from the corresponding sodium salts by reaction with $AgNO_3$. ^1H NMR spectra were recorded on a JEOL EX 270 (270 MHz) spectrometer, using $CDCl_3$ as solvent and referenced to residual $CHCl_3$, with chemical shifts being reported as δ (ppm) from tetramethylsilane, and J values measured in Hz. ^{13}C NMR (DEPT) spectra were recorded on a JEOL 270 MHz spectrometer operating at 67.8 MHz using $CDCl_3$ as solvent and reference (δ 77.0). ^1H and ^{13}C nuclei corresponding to aromatic groups associated with the ester ligands are annotated Ph′ and C′ respectively. IR spectra were recorded on a Perkin-Elmer Spectrum BX FTIR spectrophotometer. Elemental analyses were conducted by the University of Warwick analytical service.

Preparations

$SbPh_3[O_2CC(OH)Ph_2]_2$ 3a. The silver salt of $HO_2CC(OH)Ph_2$ **a** (992 mg, 2.96 mmol) was added to a stirred solution of $SbPh_3Cl_2$ (628 mg, 1.48 mmol) in THF (30 ml). The heterogeneous solution was stirred at room temperature for *ca.* 12 h in the absence of light. After filtration, a clear solution was obtained which was concentrated *in vacuo* (*ca.* 10 ml). After the addition of hexane (5–10 ml), the solution was allowed to stand at 0 °C, affording a white crystalline solid which was characterised as complex **3a** (86%) (Found: C, 68.4; H, 4.6. $C_{46}H_{37}O_6Sb$ requires C, 68.6; H, 4.6%); ν_{max} (KBr)/cm^{-1} 3495, 1295 (OH) and 1665 (C=O); δ_H (270 MHz, $CDCl_3$) 7.41 and 7.20 (35 H, 2 × m, Ph and Ph′); δ_C (68 MHz, $CDCl_3$) 174.7 (C=O), 143.6 (*i*-C′), 135.4 (*o*-C), 135.0 (*i*-C), 131.9 (*p*-C), 129.6 (*m*-C), 127.9

Table 5 Crystal data and refinement parameters for $SbPh_3[O_2CC(OH)Ph_2]_2$ **3a**, $SbPh_3[O_2CC_6H_4OH$-*o*$]_2$ **3b** and $BiPh_3[O_2CC(OH)Ph_2]_2$ **4a**

	3a	**3b**	**4a**
Empirical formula	$C_{46}H_{37}O_6Sb$	$C_{33}H_{26}Cl_3O_6Sb$	$C_{46}H_{37}O_6Bi$
Formula weight	807.51	894.74	746.64
Crystal system/space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$
a/Å	10.082(2)	10.102(2)	10.7855(1)
b/Å	20.406(4)	20.609(4)	17.7361(2)
c/Å	18.756(4)	18.706(4)	18.7408(2)
α/°			113.4792(7)
β/°	103.87(3)	103.59(3)	104.5722(8)
γ/°			93.1164(8)
V/Å^3	3746.2(13)	3785.4(13)	3133.74(6)
Z	4	4	4
μ/mm^{-1}	0.787	1.180	4.707
Reflections collected	51055	114627	39328
Independent reflections	7657	8685	12197
R_{int}	0.0986	0.0766	0.0399
Final $R1$, wR_2 [$I > 2\sigma(I)$] on F_o^2	0.0348, 0.0959 (6257 reflections)	0.0268, 0.0796 (7696 reflections)	0.0466, 0.1281 (10311 reflections)
(all data) on F_o^2	0.0474, 0.1072	0.0320, 0.0879	0.0560, 0.1335

(*o*-C′), 127.4 (*m*/*p*-C′) and 81.7 (C_α). Single crystals of complex **3a** suitable for X-ray analysis were grown from dichloromethane solution layered with hexane.

$SbPh_3[O_2CC_6H_4OH$-*o*$]_2$ 3b. This was prepared using a similar procedure to that described earlier for complex **3a**, using the silver salt of **b** (73%) (Found: C, 57.8; H, 3.8. $C_{32}H_{25}O_6Sb\cdot0.4CHCl_3$ requires C, 57.6; H, 3.8%); ν_{max} (KBr)/cm^{-1} 3058, 1353 (OH) and 1634 (C=O); δ_H (270 MHz, $CDCl_3$) 11.63 (2 H, s, OH), 8.07 (6 H, m, *o*-H of Ph), 7.82 (2 H, m, H-6 of C_6H_4), 7.55 (9 H, m, *m*,*p*-H of Ph), 7.35 (2 H, m, H-4 of C_6H_4) and 6.84 (4 H, m, H-3/5 of C_6H_4); δ_C (68 MHz, $CDCl_3$) 173.3 (C=O), 161.6 (C-2 of C_6H_4), 136.5 (*i*-C), 134.9 (C-4 of C_6H_4), 133.7, 129.8 (*o*/*m*-C), 131.7 (*p*-C), 130.7 (C-6 of C_6H_4), 118.6 (C-5 of C_6H_4), 117.1 (C-3 of C_6H_4) and 114.6 (C-1 of C_6H_4). Single crystals of **3b** suitable for X-ray analysis were grown from a concentrated chloroform solution.

$BiPh_3[O_2CC(OH)Ph_2]_2$ 4a. This was prepared using the same procedure as described for complex **3a**, using the silver salt of **a** (63%) (Found: C, 61.8; H, 4.2. $C_{46}H_{37}BiO_6$ requires C, 61.7; H, 4.1%); ν_{max} (KBr)/cm^{-1} 3483, 1328 (OH) and 1625 (C=O); δ_H (270 MHz, $CDCl_3$) 7.79 (6 H, m, *o*-H of Ph), 7.46 (9 H, m, *m*,*p*-H of Ph), 7.18 (20 H, *o*,*m*,*p*-H of Ph) and 4.54 (2 H, s, OH); δ_C (68 MHz, $CDCl_3$) 178.1 (C=O), 157.4 (*i*-C), 143.4 (*i*-C′), 133.8, 131.5 (*o*,*m*-C), 131.3 (*p*-C), 127.6, 127.4 (*o*,*m*-C′), 127.2 (*p*-C′) and 81.2 (C_α). Single crystals of **4a** suitable for X-ray analysis were grown from a concentrated chloroform solution.

$BiPh_3[O_2CC_6H_4OH$-*o*$]_2$ 4b. This was prepared using the same procedure as described for complex **3a** using $BiPh_3Cl_2$ (82%) (Found: C, 53.8; H, 3.5. $C_{32}H_{25}BiO_6$ requires C, 53.8; H, 3.5%); ν_{max} (KBr)/cm^{-1} 3052, 1389 (OH) and 1626 (C=O); δ_H (270 MHz, $CDCl_3$) 11.59 (2 H, s, OH), 8.25 (6 H, d, *J* 7.5, *o*-H of Ph), 7.83 (2 H, m, H-6 of C_6H_4), 7.63 (6 H, t, *J* 7.5, *m*-H of Ph), 7.49 (3 H, t, *J* 7.5, *p*-H of Ph), 7.32 (2 H, m, H-4 of C_6H_4), 6.86 (2 H, m, H-3 of C_6H_4) and 6.78 (2 H, m, H-5 of C_6H_4); δ_C (68 MHz, $CDCl_3$) 174.9 (C=O), 161.3 (C-2 of C_6H_4), 159.2 (*i*-C), 134.6 (C-4 of C_6H_4), 133.9, 131.6 (*o*/*m*-C), 131.3 (*p*-C), 131.1 (C-6 of C_6H_4), 118.4 (C-5 of C_6H_4), 116.9 (C-3 of C_6H_4) and 114.9 (C-1 of C_6H_4).

Data retrieval

Crystal structures containing appropriate molecular fragments were located within the Cambridge Structural Database (CSD)[28] using the QUEST program. Data for these molecular structures were retrieved from the October 1999 release of the CSD in which the master data file contained 207,507 entries.

Molecular modelling calculations

Molecular modelling calculations were conducted using the Chem-X package (1999.2) supported on the Windows NT platform using a Pentium personal computer. The van der Waals energy (E_{vdW}) calculation within Chem-X is a subset of the full molecular mechanics calculation which assumes that all bond lengths and angles are fixed and idealised and that the energy depends only upon the non-bonded (including 1,4) interactions. For all calculations idealised structures have been used, with average bond lengths and angles being derived from the appropriate crystallographic data. Phenyl rings were treated as rigid bodies of D_{6h} symmetry. The van der Waals energy (E_{vdW}) involves contributions from the torsion (V_{tor}), electrostatic (V_{el}), and non-bonded (V_{nb}) terms [as defined in eqn. (1)],

$$E_{vdW} = V_{tor} + V_{el} + V_{nb} \qquad (1)$$

but without the range of functional forms and parameters for Bi and Sb. Consequently, the calculations described herein can only be viewed as qualitative in nature.

Generic barrier constants were employed in the basic form of the torsion term (V_{tor}). The electrostatic contribution (V_{el}) is computed as a monopole–monopole interaction using Coulomb's law. The van der Waals interaction potential (V_{nb}) within the software package is that of Del Re *et al.*,[29] and takes the form given in eqn. (2).

$$V_{nb} = [A\exp(-Br)]r^{-D} - Cr^{-6} \qquad (2)$$

In all calculations, steric contributions to V_{nb} from the metal atom were not included because of the lack of adequate parameterisation. The van der Waals energy was minimised for all conformations by independent rotations about all other single bonds (except those to hydrogen atoms) within the molecule.

Crystallography

A summary of data collection and refinement parameters for compounds **3a**, **3b** and **4a** is presented in Table 5.

Data collection and structure refinement. Data were collected on a Nonius KappaCCD area detector diffractometer (150 K) controlled by the Collect[30] software package.[31] Corrections for absorption were applied using the empirical method employed in Sortav.[32] The structure was solved by direct methods (SHELXS 97[33]) and then subjected to full-matrix least squares refinement based on F_o^2 (SHELXL 97). Non-hydrogen atoms were refined anisotropically with hydrogens included in idealised positions.

CCDC reference number 186/1998.

See http://www.rsc.org/suppdata/dt/b0/b002337j/ for crystallographic files in .cif format.

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