Upon the Intriguing Stereoselective Formation of Organobismuth(V) Complexes

Hubert Barucki,[a] Simon J. Coles,[b] James F. Costello,*[a] and Michael B. Hursthouse[b]

Abstract: The preparation of triphenylbismuth(v) **3a**–**k** and antimony(v) **4e**–**k** bis-carboxy ester complexes is described. A range of studies in solution suggest that the diastereoselective formation of (*RR*,*SS*)-**3a**–**j** is governed by the thermodynamic stability of rapidly interconverting epimeric species. Diastereoselectivity is absent in the case of the corresponding Sb complexes, leading to the conclusion that a combination of both ligand–ligand (steric) and metal–ligand (hyperconjugative) interactions govern stereoselectivity. The formation of homochiral complexes (*RR*,*SS*)-**3a**–**j** is rationalised using a simple model, invoking for the first time a *palindromic* $BiPh_3$ propeller moiety, which correlates the chirality of the *trans* axial carboxy-ester ligands. The X-ray crystal structures of both hetero- and homochiral diastereoisomeric antimony complexes (**4h** and **4i**, respectively) are presented in support of this model.

Keywords: antimony · bismuth · diastereoselectivity · hyperconjugation · propellers

Introduction

Molecular propellers are structures possessing two or more substituents arranged about a central helical axis, ranging in scale from the remarkable macromolecular topology of human telomeric DNA,[1] to relatively simple sterically hindered organic and organometallic compounds.[2] Since the early identification and subsequent stereochemical analyses of correlated triaryl propeller systems (i.e., Ar_3X),[3] few if any attempts have been made to investigate possible applications in synthesis, or material science *etc*. Recently, we rationalised and more importantly developed a *predictive* model for describing the preferred chiral propeller arrangements of ligands—such as the ubiquitous PPh_3—when co-ordinated to transition metal centres.[4] Related studies lead to the discovery that an inversion of the propeller conformation of co-ordinated PPh_3 induced a switch in sign of the specific rotation of stereogenic organometallic complexes.[5] Appreciating the preferred conformations of phenyl propellers helps us to understand chemical reactivity. For example, the complex $SbPh_3Cl_2 \cdot$**2** ordinarily undergoes a cyclometallation reaction with α-hydroxy carboxylates.[6] In the case of benzilic acid [$Ph_2C(OH)CO_2Ag$], however, prohibitive steric clashing involving CPh_2 and $SbPh_3$ propellers attenuates the rate of cyclometallation to such a degree that simple chloride metathesis occurs instead. Our interest in organobismuth(v) chemistry has been stimulated recently by unusual observations which indicate novel applications for such complexes as reagents for asymmetric synthesis.[7]

This report relates principally to the observations of Wang et al.,[8] who discovered that treatment of a THF solution of $BiPh_3Cl_2 \cdot$**1** with two equivalents of (±)-Ag:**b** (Table 1) afforded a *single* diastereoisomer of the corresponding bis-carboxy ester **3b** (Scheme 1). Furthermore, X-ray crystallography confirmed the stereoisomer to possess the homochiral (*RR*,*SS*) as opposed to the heterochiral (*RS*,*SR*) configuration. Examination of the analogous reaction of $Bi(C_6H_4p\text{-}NMe_2)_3Cl_2$ with (±)-Ag:**b**, (±)-Ag:**e** and (±)-Ag:**h** furnished the same conclusion; that is, the process appears to be stereoselective with respect to the formation of a homochiral bis-carboxy ester. An explanation for these observations could not be presented at the time. However, it appeared to us that a correlated, *palindromic* arrangement of the $BiPh_3$ system must be involved in the formation of a *homochiral* isomer. In this study, we describe the preparation of a variety of complexes from **1** and **2**, to examine the role of both steric and electronic effects upon the diastereoselective formation of **3b**, for example. A variety of experiments have been carried out in order to establish the kinetic/thermodynamic basis for stereoselectivity. Having established this, we conclude by describing a simple model consistent with calcula-

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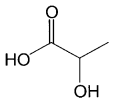
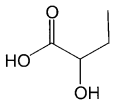
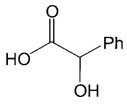
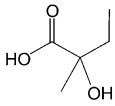
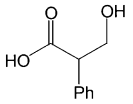
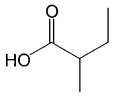
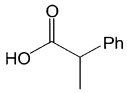
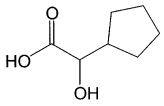
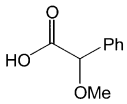
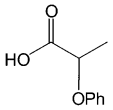
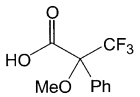
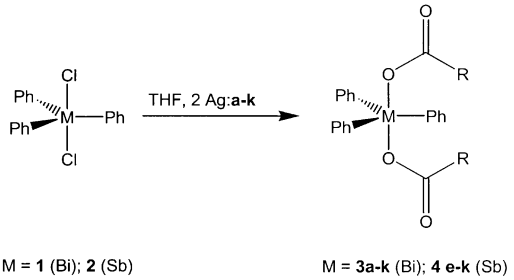
Table 1. Carboxylic acids **a**–**k**, and the corresponding stereochemical assignments for **3a**–**k** and **4e**–**k**.

	Acid	Metal	
		3·[Bi]	**4**·[Sb]
a		(*RR*,*SS*)	–[a]
b		(*RR*,*SS*)	–[a]
c		(*RR*,*SS*)	–[a]
d		(*RR*,*SS*)	–[a]
e		(*RR*,*SS*)	(*RR*,*SS*,*RS*)
f		(*RR*,*SS*)	(*RR*,*SS*,*RS*)
g		(*RR*,*SS*)	(*RR*,*SS*,*RS*)
h		(*RR*,*SS*)	(*RR*,*SS*,*RS*)
i		(*RR*,*SS*)	(*RR*,*SS*,*RS*)
j		(*RR*,*SS*)	(*RR*,*SS*,*RS*)
k		(*RR*,*SS*,*RS*)	(*RR*,*SS*,*RS*)

[a] Cyclometallation observed.[6]



Scheme 1. Complex preparation.

tions and X-ray crystallographic data, which rationalises this intriguing stereoselectivity. For the first time, we propose that a chiral *palindromic* propeller arrangement facilitates the formation of a homochiral diastereoisomeric complex.

Results

It is well known that both $BiPh_3Cl_2$ and $SbPh_3Cl_2$ (**1** and **2**, Scheme 1) undergo metathetical reactions with the silver salts of carboxylic acids to afford bis-carboxy esters **3**–**4**.[9] Here, complexes **3a**–**k** and **4e**–**k** were prepared by stirring a THF solution of **1**–**2** with a two-fold excess of the silver salts of **a**–**k** (Table 1) for 2 h under nitrogen. The resulting bis-carboxy esters were characterised using $^1H/^{13}C$ NMR, IR spectroscopy, elemental analyses and where possible X-ray crystallography. Parent ions eluded detection by low resolution EI, CI, FAB and electrospray mass spectrometry techniques. In contrast with **1**, the antimony complex **2** reacts with α-hydroxy carboxylates Ag:(±)-**a**–**d** to afford cyclometallated complexes, which have been discussed elsewhere.[6]

Stereochemical assignments for **3a**–**k** and **4e**–**k** are summarised in Table 1. Salts Ag:(±)-**a**–**d** appear to react with **1** to afford **3a**–**d** as a single diastereoisomer. NMR analyses across a range of field strengths (300–400 and 68–100 MHz for ^1H and ^{13}C, respectively), temperatures (213–273 K) and solvents ($CDCl_3$, [D_8]THF, [D_4]MeOH, [D_5]C_5H_5N and [D_6]DMSO) fail to reveal more than a single set of resonances for **3a**–**d**. A homochiral configuration (i.e., *RR*,*SS*) for **3a**–**d** is assigned on the basis of NMR and X-ray crystallographic inference. The $^1H/^{13}C$ NMR spectra of (*SS*)-**3a** for example, prepared using Ag:(*S*)-**a**, are identical to those of (*RR*,*SS*)-**3a**. Furthermore, the X-ray crystal structure of the tris(*p*-$NMe_2C_6H_4$) analogue of (*RR*,*SS*)-**3b**[8a] has been solved on several occasions, and in each case the homochiral diastereoisomer is observed.

It has been reported that **1** reacts with Ag:(±)-**e** to afford **3e** as a single diastereoisomer.[8] X-ray crystallographic analyses of both **3e** and the corresponding tris(*p*-$NMe_2C_6H_4$) analogue confirm a homochiral configuration in each case.[8b] In contrast, resonance anisochronicity in the ^{13}C NMR spectrum of **4e** (i.e., C_i, C_α and C_β suggest that **2** affords a mixture of diastereoisomers (i.e., *RR*/*SS* and *RS*/*SR*) under the same reaction conditions. The stereochemistry attributed to **3**/**4f**–**h** is similar insofar as **1** furnishes a single diastereoisomer with Ag:(±)-**f**–**h**, whereas **2** affords both diastereoisomers (i.e., *RR*/*SS* and *RS*/*SR*). Importantly, the first example of a *meso* complex (Figure 1) has been characterised by the X-ray crystal structure analysis of a single crystal of (*RS*)-**4h**, grown from a THF solution of all stereoisomers.

Carboxylates Ag:(±)-(**i**–**j**), possessing an α-ether function, react with **1** to afford **3i**–**j** as a single diastereoisomer. In contrast, the corresponding Sb complexes **4i**–**k** are formed non-stereoselectively. In the case of the latter, two resonances (assigned to C_α of the carboxy ligands) are observed in the ^{13}C NMR spectrum (in $CDCl_3$) of (*RR*,*SS*,*RS*)-**4i** ($\delta_C = 83.3$ and 83.2 ppm). Single crystals of (*SS*,*RR*)-**4i** suitable for X-ray crystallographic analyses were grown from a THF solution of (*RR*,*SS*,*RS*)-**4i** (Figure 2).[10] The reaction of Ag:(±)-**k** and **1** constitutes the first example of a non-stereoselective reaction involving this metal. Two resonances are observed in the ^{19}F NMR ($CDCl_3$) spectrum of **3k** ($\delta_F = -71.1$ and -71.2 ppm), thereby confirming the presence of all stereoisomers (i.e., *RR*,*SS*,*RS*). Enantiomerically pure (*SS*)-**3k** ($\delta_F = -71.1$ ppm),

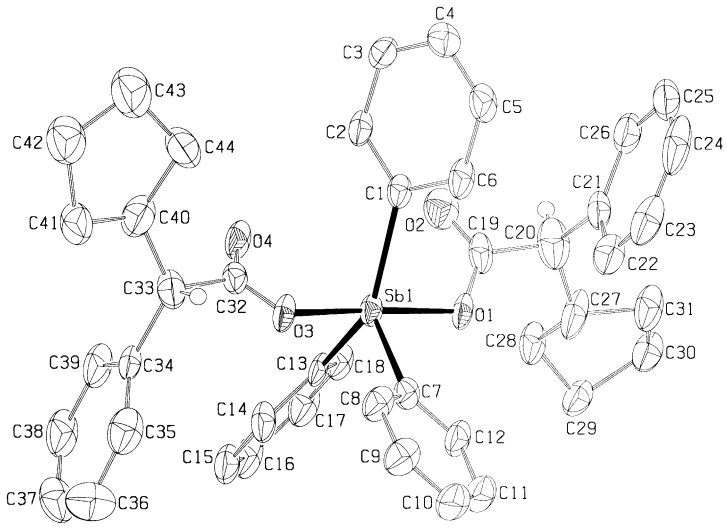


Figure 1. The molecular structure of (*RS*)-$SbPh_3[O_2CCH(C_5H_9)Ph]_2$ (**4h**), with 50% probability thermal ellipsoids.

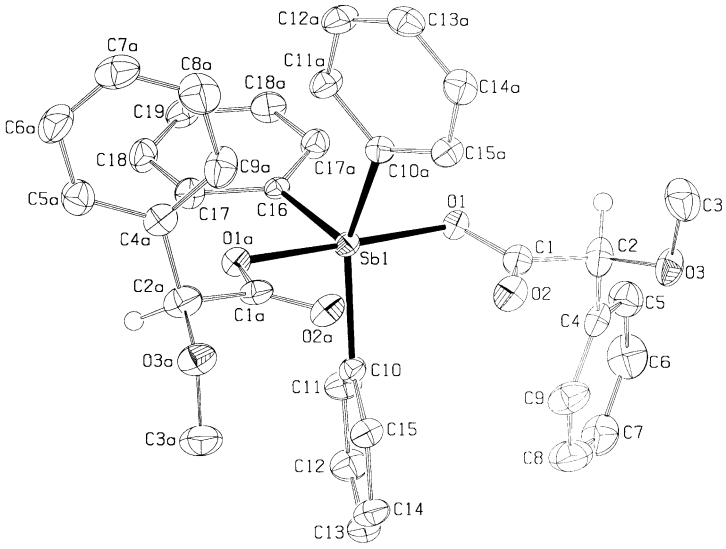


Figure 2. The molecular structure of (*SS*)-$SbPh_3[O_2CCH(OMe)Ph]_2$ (**4i**), with 50% probability thermal ellipsoids.

Table 2. Selected bond lengths [Å] and angles [°] for complexes **4h** and **4i**.

4h		**4i**	
Sb1-C1	2.283(5)	Sb1–C10	2.122(2)
Sb1–C7	2.152(6)	Sb1–C16	2.093(3)
Sb1–C13	1.952(4)	–	–
Sb1–O1	2.137(3)	Sb1–O1	2.1319(15)
Sb1–O3	2.151(3)	–	–
O1-Sb1-O3	175.84(12)	O1-Sb1-O1[a]	178.39(7)
C1-Sb1-O1	84.94(15)	C10-Sb1-O1	88.55(7)
C1-Sb1-O3	96.14(15)	C10-Sb1-O1[a]	91.89(7)
C1-Sb1-C7	123.08(17)	C10-Sb1-C16	105.81(6)
C1-Sb1-C13	138.06(19)	C10-Sb1-C10[a]	148.37(11)
C7-Sb1-O1	98.36(13)	C16-Sb1-O1	89.20(4)
C7-Sb1-O3	77.67(17)	–	–
C7-Sb1-C13	98.9(2)	–	–
C13-Sb1-O1	88.78(16)	–	–
C13-Sb1-O3	93.06(17)	–	–

[a] Generated by the symmetry operation $(-x, y, -z+0.5)$.

prepared using Ag:(*S*)-**k**, allows the unambiguous assignment of both diastereoisomers to be made.

To summarise, the organobismuth complex **1** appears to react diastereoselectively with a variety of α-chiral carboxylic acids (±)-**a**–**j**, affording the *homochiral* isomers.[11] Only one exception to this trend has been observed, that is, (±)-**k**. Complex **2** reacts in a non-stereoselective fashion with the corresponding series of acids, namely (±)-**e**–**k**; α-hydroxy derivatives lead to cyclometallated products. The structural diversity of the ligands considered here fails to implicate hydrogen bonding or $\pi-\pi$ type interactions in the process of stereoselection. However, it is certain that both the nature of the metal centre, and the observation of a homo-, as opposed to a heterochiral diastereoisomer are both significant factors to be taken into account when attempting to formulate an explanation for this intriguing example of diastereoselectivity.

Discussion

Kinetic or thermodynamic control? It has been recognised for some time that complexes related to **1**–**2** undergo rapid ligand redistribution in a variety of solvents.[12] In the case of phenoxide adducts $BiPh_3(OAr)_2$, mixed ligand species have been crystallised directly from an equilibrating solution of $BiPh_3Br_2$ and $BiPh_3(OAr)_2$.[13] We and others[8] have attempted to isolate mixed adducts of the type $BiPh_3(O_2CR)Cl$ without success. Nevertheless, such species are readily observed by NMR spectroscopy in a range of solvents (i.e., $CDCl_3$, $[D_8]$THF, and $[D_8]C_6H_5CH_3$).

Attention turns to the simplest system for study. NMR indicates that mixing **1** with an excess of AgOAc suspended in $[D_8]$THF results in the rapid formation of $BiPh_3(OAc)_2$ (**3**) (Figure 3; R = Me) and a fourth component characterised as $BiPh_3(OAc)Cl$ (**5**) by additional resonances attributed to the Bi–Ph [$\delta_H = 8.27$ (d, H_o), $\delta_C = 133.6$ (C_o), 159.0 (C_i), 133.8 (C_m) and 128.1 ppm (C_p)] and CH_3 ($\delta_H = 1.83$ and δ_C 21.6 ppm) moieties. Thorough mixing of the suspension results in the smooth and quantitative conversion of **1** and **5** to **3**. ^{1}H NMR indicates the formation of trace amounts of HOAc. However, THF and $CHCl_3$ solutions of **1** remain unaffected after several hours in the presence of HOAc; this indicates that under these conditions the free acid does not act as a nucleophile towards **1**.[14]

In isolation, the ^{1}H/^{13}C NMR spectra of **1** and $BiPh_3(OAc)_2$ remain essentially unchanged throughout the temperature range 293 → 213 K ($[D_8]$THF). However, the NMR spectra of $BiPh_3(OAc)_2$ and **1** at equilibrium are markedly affected. The

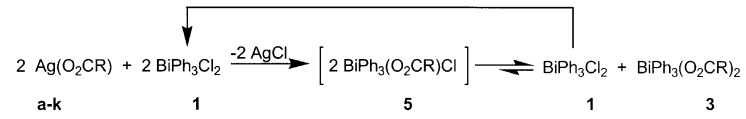
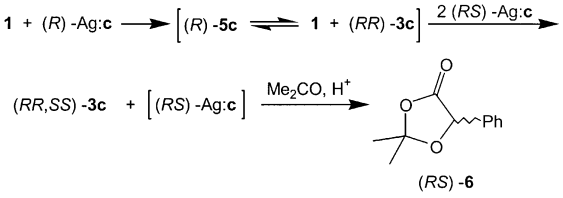


Figure 3. Ligand redistribution.

upper limb of the AA′ spin system attributed to H_o for all species exhibits splitting at 293 K. The resonance associated with the CH_3 moiety of $BiPh_3(OAc)Cl$ splits at 253 ($\delta_H = 1.83$ ppm) and 233 K ($\delta_C = 21.6$ ppm), respectively. Further resonance splitting attributed to $BiPh_3(OAc)_2$ (C_i, 253 K), $BiPh_3(OAc)Cl$ (C_i, 253 K) and **1** (C_m, 253 K) is also observed, and significantly an additional CH_3 environment is evident at 233 K ($\delta_C = 19.7$ ppm). The resonance anisochronicity, which is concentration dependent, in concert with the appearance of an additional CH_3 environment at 233 K, suggests that ligand exchange may proceed *via* some aggregate, possibly involving the well-characterised inter-penetrating Cl/OAc ligand motif.[15] NMR and thermodynamic measurements upon the exchange reactions of $SbMe_3XY$ [X, Y = Cl, Br, OAc, $O_2CCH_{3-n}Cl_n$ ($n = 0-3$)] are consistent with the participation of bridged intermediates.[16] The adduct generated by mixing (*RR*,*SS*)-**3a** and **1** is readily identified by NMR resonances at $\delta_C = 157.7$ (C_i), 133.8 (C_o) and 20.5 ppm (CH_3) ([D_8]THF). The latter resonance splits at 253 or 233 K, depending upon the concentration [1.0 – 0.5 M]. Importantly, NMR spectroscopy allows the formation of (*RR*,*SS*)-**3a – c** (and **3g – j**) to be observed in situ, thereby discounting the operation of a crystallisation induced asymmetric transformation.[17]

It is difficult to study the mixed ligand species **5** in isolation as it exists in dynamic equilibrium with **1** and **3**. Nevertheless, the proposition that enantiomerically pure **5** expresses chiral discrimination when reacting with a racemic carboxylate salt is readily challenged as follows (Scheme 2). A solution



Scheme 2.

containing a single enantiomer of **5** was prepared by mixing equimolar quantities of (*R*)-(Ag:**c**) and **1** in THF. To this solution was added a two-fold excess of Ag:(±)-**c**. If indeed (*R*)-**5c** reacts in a diastereoselective fashion with Ag:(±)-**c** to afford (*RR*)-**3c**, an enantiomerically enriched sample of unreacted Ag:(±)-**c** will remain. The residual silver salts were recovered from such a reaction, and after acidolysis in acetone, the enantiomeric excess of ketal **6** was found to be zero. Clearly, (*R*)-**5c** fails to resolve Ag:(±)-**c**, indicating that **1** reacts unselectively with Ag:(±)-**c** to afford (*RS*)-**5c** which in turn undergoes a series of ligand re-distribution reactions to afford **1**, and (*RR*,*SS*)-**3c**. The process is driven to completion by the consumption of **1**. The redistribution of constitutionally identical ligands is readily demonstrated using **3k**. Samples of enantiomerically pure (*RR*)-**3k** and (*SS*)-**3k** were prepared using (*R*)-Ag:**k** and (*S*)-Ag:**k**, respectively. ^{19}F NMR illustrates the formation of both hetero-(*SR*)-**3k** and homochiral (*RR*,*SS*)-**3k** complexes immediately upon mixing solutions of (*RR*)-**3k** and (*SS*)-**3k**. To summarise, the diastereoselectivity observed in the formation of **3a – j** is governed by the thermodynamic stability of rapidly interconverting epimeric species (*RR*,*SS*)-**3a – j** and (*SR*,*RS*)-**3a – j**. As diastereoselectivity is not observed for the corresponding Sb complexes **4e – k**, it must be concluded that a combination of both ligand – ligand and metal – ligand interactions govern stereoselectivity.

Rationalising diastereoselectivity: The preferred arrangement of a tri-aryl system is governed both by inter ring – ring and inter ring – ligand steric interactions.[18] Calculations and X-ray crystallographic studies demonstrate[19] that the equatorial phenyl ligands within the *trigonal bipyramidal* (TBPY) complexes **1 – 2** prefer to adopt the enantiomeric (*P*)/(*M*) propeller arrangement (Figure 4). Both the (*P*) and (*M*) arrangements possess a C_2 axis of symmetry, thereby affording cylindrical helicity that is *palindromic*.[20] As defined here, a *palindromic* cylindrical helix reads the same irrespective of which Cl–M bond the molecule is viewed. The formation of *homo*- as opposed to *heterochiral* diastereoisomeric complexes therefore implicates the participation of a *palindromic* propeller system in the formation of bismuth complexes **3a – j**.

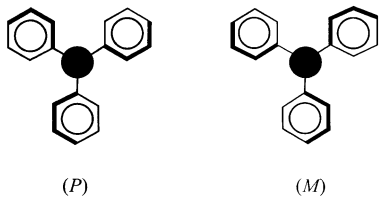


Figure 4. Projections (viewed along the Cl–M bond) of the degenerate, *palindromic* propeller conformations adopted by **1 – 2**.

Figure 5b depicts a TBPY complex of type **3** (viewed along the O–Bi bond) in which the equatorial phenyl ligands A – C adopt a correlated *M* propeller. The closed circle depicts the commonly encountered *cis* arrangement of carboxy ligands. The orientation of both σ_{nb} donating C=O groups approximately *anti* to the Bi–C_{ipso} bond of ring A affords a propitious geometrical arrangement for $\sigma_{nb} \rightarrow \sigma_{Bi}^*$ orbital overlap.[19] Calculations and X-ray structural correlations suggest that despite being sterically strained, the *cis* arrangement depicted here is in fact favoured because of stabilising[21] Bi···O=C ($\sigma_{nb} \rightarrow \sigma_{Bi}^*$) interactions. The X-ray crystal structures of stereogenic complexes **3e** and the tris(p-$NMe_2C_6H_4$) analogues of **3b** and **3e** also adopt the arrangement depicted in Figure 5b. Equilibrium constants [$MPh_3Cl_2 + MPh_3(O_2CR)_2 \leftrightarrow 2\,MPh_3(O_2CR)Cl$] for the redistribution of Cl and OAc in **1 – 2** were calculated to examine the participation of such stabilising effects in solution.[22] The Bi complex demonstrates a near

statistical distribution of species [$K(\mathrm{Bi}) = 0.8 \pm 0.1$], whereas the analogous Sb complex exhibits a preference for the mixed-ligand adduct $MPh_3(O_2CR)Cl$ [$K(\mathrm{Sb}) = 1.7 \pm 0.1$]. The trend extends to ligands **e** [$K(\mathrm{Bi}) = 1.3 \pm 0.1$; $K(\mathrm{Sb}) = 1.8 \pm 0.1$] and **g** [$K(\mathrm{Bi}) = 3.1 \pm 0.1$; $K(\mathrm{Sb}) = 10.0 \pm 0.1$]. It would seem that in solution, the bis-carboxy complexes of Bi are stabilised relative to the corresponding Sb species. Calculations[23] demonstrate that the LUMOs of **1**–**2** for example, are situated mainly on the metal centre, and as anticipated[24] the energy of $\sigma^*_{\mathrm{Bi–C}}$ is about 100 kJ mol^{-1} less than that of the corresponding $\sigma^*_{\mathrm{Sb–C}}$. Evidently, the overlap of C=O σ_{nb} and $\sigma^*_{\mathrm{Bi–C}}$ orbitals produces a greater stabilising affect than the corresponding Sb-centred interaction.

Projections of an α-stereogenic carboxy-ester possessing large (L), medium (M) and small (S) groups (arbitrarily assigned *S* and *R*) are presented in Figure 5a and c, respectively. The *S* carboxy-ester (Figure 5a) orients L above the sterically undemanding face of ring C. However, the *R* configuration (Figure 5c) orients L proximal to the sterically demanding edge of ring B, which is anticipated to be disfavoured. Consequently, as defined here the *S* carboxy-ester favours the *M* propeller arrangement of the $BiPh_3$ moiety. Given the *palindromic* nature of the $BiPh_3$ moiety, a complementary configuration of co-ordinated carboxy esters is therefore preferred that is, *homochiral* (*S*-*M*-*S*) as opposed to the alternative *heterochiral* (*S*-*M*-*R*) arrangement. A similar argument applies to the degenerate *P* propeller configuration, where the configurational preference decreases in the order (*R*-*P*-*R*) > (*S*-*P*-*R*) > (*S*-*M*-*S*). The X-ray crystal structures of (*SR*)-**4h** and (*SS*)-**4i** (Figures 1 and 2, respectively, and indeed **3e** and the tris(p-$NMe_2C_6H_4$) analogues of **3b** and **3e**) are consistent with this model. Firstly, the $SbPh_3$ unit of (*SS*)-**4i** adopts a correlated *M* propeller arrangement [i.e., (*S*-*M*-*S*) Figure 5b]. As anticipated, the propeller is sandwiched by a complementary pair of *cis* disposed (*S*) carboxy ligands (i.e., Figure 5a, L = Ph, M = OMe and S = H). Strong non-bonded interactions are characterised by Sb···O=C 2.80 Å.

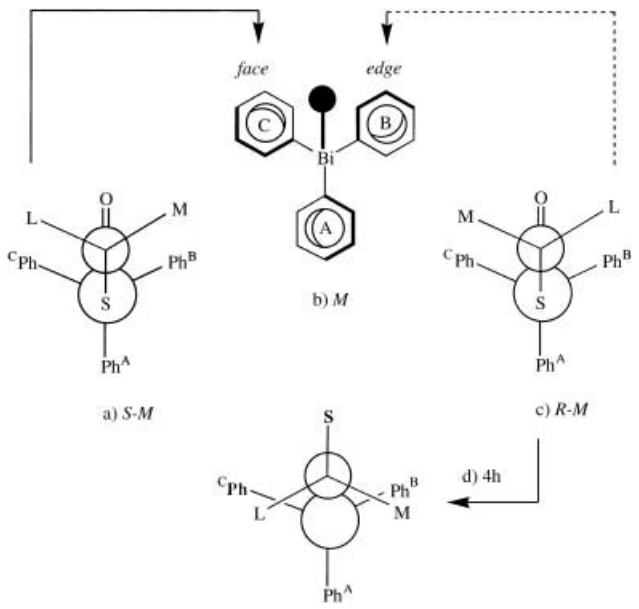


Figure 5. Diastereoselection by a *palindromic* molecular propeller. The closed circle of (b) represents the C = **O** atom above the plane of the equatorial phenyl ligands.

The X-ray crystal structure of the *meso* complex (*SR*)-**4h** (Figure 1) also adopts the *cis* arrangement as depicted in Figure 5b. As expected, the (*S*) carboxy ester (i.e., L = Ph, M = C_5H_9 and S = H) and the *M* propeller adopt the complementary arrangement depicted in Figure 5a. However, distortions attend the non-complementary (*R*) ester. The anticipated steric clashing associated with the (*S*-*M*-*R*) combination (i.e., Ph vs the edge of ring B, Figure 5c) is circumvented by a 180° rotation about the OC–C_α bond, thereby orienting L (Ph) proximal to ring C (Figure 5c, d). The attendant structural distortions prevent the *mismatched* carboxy ester from participating in a secondary bonding interaction (Sb···O=C 3.60 Å).

We have demonstrated previously the correlation between the pK_a of a parent carboxylic acid, and the crystallographically determined M···O=C distance within **3**–**4**.[19] In the case of **4** for example, a parent acid with p$K_a \leqslant 2.8$ does not participate in secondary bonding interactions (Sb···O=C > 3.2 Å) and subsequently fails to stabilise the commonly encountered, and sterically strained *cis* arrangement. This observation is consistent with the bonding model outlined earlier, in which an electron withdrawing substituent "R" (Figure 6) serves to attenuate $\sigma_{\mathrm{nb}} \rightarrow \sigma_{\mathrm{M–C}}{}^*$ overlap. The stereoselectivity observed for the series of complexes (*RR*,*SS*)-**3c** (p$K_a \approx 3.8$), (*RR*,*SS*)-**3i** (p$K_a \approx 2.8$) and (*RR*,*SS*,*RS*)-**3k** (p$K_a \approx 1.0$)[25] would appear to suggest that the -CF_3 group of **k** is sufficiently electron withdrawing to destabilise the strained conformation required to correlate *trans* carboxy ligands within **3k**.

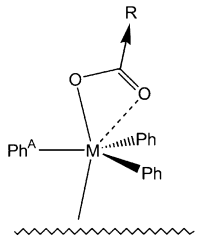


Figure 6. Asymmetric bidentate bonding destabilised by electron withdrawing "R".

Conclusion

The diastereoselective formation of the homochiral organobismuth complexes **3a**–**j** is believed to proceed by a relatively strained *palindromic* chiral propeller arrangement, stabilised by intramolecular $\sigma_{\mathrm{nb}} \rightarrow \sigma^*_{\mathrm{Bi–C}}$ orbital interactions. The model used to rationalise stereoselectivity is consistent with calculations and empirical data derived from X-ray crystallography. Calculations, X-ray crystallographic studies and equilibrium measurements indicate that the $\sigma_{\mathrm{nb}} \rightarrow \sigma^*_{\mathrm{M–C}}$ interactions of Sb are less stabilising than those of the corresponding Bi complexes. The difference in complex stability appears to be sufficient for the corresponding organoantimony complexes **4e**–**k** to be formed non-stereoselectively. Similarly, the carboxy ligand within the organobismuth complex **3k**, appears to provide insufficient electron density to afford stabilising $\sigma_{\mathrm{nb}} \rightarrow \sigma^*_{\mathrm{Bi–C}}$ orbital interactions, and thereby furnish a single, *homochiral* diastereoisomer.

Experimental Section

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 $AgNO_3$. ^{1}H NMR spectra were recorded on either a JEOL Eclipse + 300 (300 MHz) or a Bruker DPX400 (400 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 either a JEOL Eclipse + 300 (75 MHz) or a Bruker DPX400 (100 MHz) spectrometer. ^{13}C NMR signal splitting means resonance anisochronicity of the order 3–8 Hz, and is attributed to the presence of two diastereoisomers (i.e., *RR*,*SS*,*SR*). All signals are reported for splitting > 8 Hz. ^{19}F NMR spectra were recorded on a Jeol Eclipse + 300 (283 MHz) spectrometer. IR spectra were recorded on a Perkin Elmer Spectrum BX FTIR spectrophotometer. Elemental analyses were conducted by the University of Warwick analytical service. Gas chromatography was conducted on a Schimadzu GC-17A instrument using a Chiraldex G-TA column (30 m × 0.25 mm).

(*RR*,*SS*)-BiPh$_3$[O$_2$CCH(OH)Me]$_2$ (3a): The silver salt of lactic acid (*R*,*S*)-**a** (231 mg, 1.17 mmol) was added to a solution of **1** (300 mg, 0.59 mmol) in THF (20 mL) and stirred at room temperature for ca. 2 h in the absence of light. After filtration, a clear solution was obtained which was concentrated in vacuo (ca. 10 mL). Hexane was added (5–10 mL) and the solution was allowed to stand at 0 °C, affording a white crystalline solid characterised as **3a** (72 %). IR (KBr): $\tilde{\nu}$ = 3497, 1296, 1604 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.10 (d, 6H, J = 7.0 Hz), 7.63 (t, 6H, J = 7.0 Hz), 7.50 (t, 3H, J = 7.0 Hz), 4.03 (q, 2H, J = 7.0 Hz), 2.99 (br s, 2H), 1.12 (d, 6H, J = 6.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.6, 158.7, 133.9, 131.5, 131.3, 67.4, 20.7; elemental analysis calcd (%) for $C_{24}H_{25}BiO_6$ (618.2): C 46.6, H 4.1; found: C 46.8, H 4.0.

(*RR*,*SS*)-BiPh$_3$[O$_2$CCH(OH)Et]$_2$ (3b): Prepared using the same procedure as described for **3a** using the silver salt of (*R*,*S*)-**b** (67 %). IR (KBr): $\tilde{\nu}$ = 3482, 1324, 1619 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.12 (d, 6H, J = 7.5 Hz), 7.63 (t, 6H, J = 7.5 Hz), 7.52 (t, 3H, J = 7.5 Hz), 3.92 (br m, 2H), 2.91 (br s, 2H), 1.57, 1.42 (2 × m, 4H), 0.56 (t, 6H, J = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.0, 159.1, 134.1, 131.4, 131.3, 71.8, 27.6, 8.4; elemental analysis calcd (%) for $C_{26}H_{29}BiO_6$ (646.3): C 48.3, H 4.5; found: C 47.9, H 4.5.

(*RR*,*SS*)-BiPh$_3$[O$_2$CCH(OH)Ph]$_2$ (3c): Prepared using the same procedure as described for **3a**, using the silver salt of (*R*,*S*)-**c** (74 %). IR (KBr): $\tilde{\nu}$ = 3473, 1297, 1625 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.73 (m, 6H), 7.46 (m, 9H), 7.20 (m, 10H), 4.95 (d, 2H, J = 5.0 Hz), 3.62 (d, 2H, J = 5.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.4, 156.9, 140.1, 133.7, 131.5, 131.2, 128.1, 126.4, 127.5, 73.6; elemental analysis calcd (%) for $C_{34}H_{29}BiO_6$ (742.3): C 55.0, H 3.9; found: C 54.6, H 3.9.

(*RR*,*SS*)-BiPh$_3$[O$_2$CC(OH)(Me)Et]$_2$ (3d): Prepared using the same procedure as described for **3a**, using the silver salt of (*R*,*S*)-**d** (81 %). IR (KBr): $\tilde{\nu}$ = 3482, 1324, 1619 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.13 (d, 6H, J = 8.0 Hz), 7.63 (m, 6H), 7.50 (m, 3H), 3.40 (br s, 2H), 1.59, 1.45 (2 × m, 4H), 1.14 (s, 6H), 0.45 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.1, 159.3, 133.9, 133.3, 131.1, 75.0, 33.1, 26.1, 7.6; elemental analysis calcd (%) for $C_{28}H_{33}BiO_6$ (674.3): C 49.8, H 4.9; found: C 49.8, H 4.9.

(*RR*,*SS*)-BiPh$_3$[O$_2$CCH(Ph)CH$_2$OH]$_2$ (3e): see ref. [8].

(*RR*,*SS*)-BiPh$_3$[O$_2$CCH(Me)Et]$_2$ (3f): Prepared using the same procedure as described for **3a**, using the silver salt of (*R*,*S*)-**f** (80 %). IR (KBr): $\tilde{\nu}$ = 1674 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.15 (d, 6H, J = 8.0 Hz), 7.55 (m, 6H), 7.44 (m, 3H), 2.12 (q, 2H, ^3J = 6.7 Hz), 1.42, 1.22 (2 × m, 4H), 0.85 (d, 6H, J = 6.7 Hz), 0.53 (t, 6H, J = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 183.2, 161.5, 134.0, 130.9, 130.5, 42.0, 27.4, 17.3, 11.5; elemental analysis calcd (%) for $C_{28}H_{33}BiO_4$ (642.3): C 52.3, H 5.1; found: C 51.8, H 4.9.

(*RR*,*SS*)-BiPh$_3$[O$_2$CCH(Me)Ph]$_2$ (3g): Prepared using a similar procedure to that described earlier for **3a**, using the silver salt of (*R*,*S*)-**g** (65 %). IR (KBr): $\tilde{\nu}$ = 1650 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (m, 6H), 7.41 (m, 10H), 7.11 (m, 9H), 3.53 (q, 2H, ^3J = 6.7 Hz), 1.26 (d, 6H, ^3J = 6.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.7, 159.6, 142.1, 133.8, 130.4, 130.0, 128.1, 127.4, 126.1, 46.6, 18.9; elemental analysis calcd (%) for $C_{36}H_{33}BiO_4$ (738.4): C 58.5, H 4.5; found: C 57.2, H 4.4.

(*RR*,*SS*)-BiPh$_3$[O$_2$CCH(C$_5$H$_9$)Ph]$_2$ (3h): Prepared using the same procedure as described for **3a** using the silver salt of (*R*,*S*)-**h** (84 %). IR (KBr): $\tilde{\nu}$ = 1663 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (m, 6H), 7.38 (ms, 9H), 7.13 (br s, 10H), 3.12 (d, 2H, J = 11 Hz), 2.40 (m, 2H), 1.50–1.30, 0.90 (2 × m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.4, 160.2, 140.2, 133.6, 130.8, 130.2, 128.2, 127.9, 126.1, 59.1, 43.5, 31.0, 30.6, 25.2, 24.9; elemental analysis calcd (%) for $C_{44}H_{45}BiO_4$ (846.2): C 62.4, H 5.3; found: C 62.4, H 5.3.

(*RR*,*SS*)-BiPh$_3$[O$_2$CCH(OMe)Ph]$_2$ (3i): Prepared using the same procedure as described for **3a**, using the silver salt of (*R*,*S*)-**i** (71 %). IR (KBr): $\tilde{\nu}$ = 2823, 1722, 1681 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (m, 6H), 7.41 (m, 9H), 7.17 (m, 10H), 4.60 (s, 2H), 3.19 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.5, 158.4, 137.7, 134.0, 131.2, 130.7, 128.2, 127.7, 127.1, 83.6, 57.0; elemental analysis calcd (%) for $C_{36}H_{33}BiO_6$ (770.2): C 56.1, H 4.3; found: C 53.8, H 4.2.

(*RR*,*SS*)-BiPh$_3$[O$_2$CCH(OPh)Me]$_2$ (3j): Prepared using the same procedure as described for **3a** using the silver salt of (*R*,*S*)-**j** (75 %). IR (KBr): $\tilde{\nu}$ = 1670 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (m, 6H), 7.49 (m, 9H), 7.03 (m, 4H), 6.83 (m, 2H), 6.57 (d, 4H, J = 7.6 Hz), 4.49 (q, 2H, J = 6.6 Hz), 1.32 (d, 6H, J = 6.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.4, 158.0, 157.8, 134.3, 132.8, 131.9, 129.4, 121.0, 114.8, 72.9, 18.7; elemental analysis calcd (%) for $C_{36}H_{33}BiO_6$ (770.3): C 56.1, H 4.3; found: C 55.6, H 4.1.

(*RR*,*SS*,*RS*)-BiPh$_3$[O$_2$CC(CF$_3$)(OMe)Ph]$_2$ (3k): Prepared using the same procedure as described for **3a**, using the silver salt of (*R*,*S*)-**k** (80 %). IR (KBr): $\tilde{\nu}$ = 1646, 1346, 1259, 1185 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (d, 6H, J = 8.0 Hz), 7.58 (m, 9H), 7.19 (m, 2H), 7.07 (m, 8H), 3.23, 3.22 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.9, 158.1*, 134.5*, 133.9, 131.5, 131.4, 128.6, 127.7, 127.2, 123.9 (q, $^1J_{C,F}$ = 287 Hz), 84.5 (q, $^2J_{C,F}$ = 27 Hz), 54.8; ^{19}F NMR (283 MHz, $CDCl_3$): δ = −71.1, −71.2 (2 × s); elemental analysis calcd (%) for $C_{36}H_{31}BiO_6F_6$ (882.0): C 50.3, H 3.4; found: C 49.5, H 3.4. *Splitting observed.

The diastereoisomers (*SS*)- and (*RR*)-**3k** were prepared using the silver salts of (*S*)- and (*R*)-**k**, respectively. (*SS*)-**3k** (77 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.21 (d, 6H, J = 8.0 Hz), 7.58 (m, 9H), 7.19 (m, 2H), 7.08 (m, 8H), 3.22 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.0, 158.3, 134.6, 131.6, 133.8, 131.4, 128.7, 127.9, 127.3, 123.9 (q, $^1J_{C,F}$ = 287 Hz), 84.5 (q, $^2J_{C,F}$ = 27 Hz), 54.7; ^{19}F NMR (283 MHz, $CDCl_3$): δ = −71.1 (s); elemental analysis calcd (%) for $C_{36}H_{31}BiO_6F_6$ (882.0): C 50.4, H 3.4; found: C 50.2, H 3.4.

(*RR*,*SS*,*RS*)-SbPh$_3$[O$_2$CCH(Ph)CH$_2$OH]$_2$ (4e): Prepared by a similar procedure to that described earlier for **3e**, using **2** (87 %). IR (KBr): $\tilde{\nu}$ = 1769, 1644, 1354 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70 (m, 6H), 7.38 (m, 13H), 7.20 (m, 4H), 6.92 (m, 2H), 3.82, 3.60 (2 × m, 6H), 2.50 (br s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 176.4, 136.7*, 136.6, 133.7, 131.3, 129.3, 128.5, 128.3, 127.1, 64.6*, 54.8*; elemental analysis calcd (%) for $C_{36}H_{33}SbO_6 \cdot 0.4\,CHCl_3$ (682.8): C 63.2, H 4.8; found: C 59.6, H 4.6. *Splitting observed.

(*RR*,*SS*,*RS*)-SbPh$_3$[O$_2$CCH(Me)Et]$_2$ (4f): Prepared by a similar procedure to that described earlier for **3f**, using **2** (68 %). IR (KBr): $\tilde{\nu}$ = 1640 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96 (m, 6H), 7.55 (m, 9H), 2.13 (q, 2H, ^3J = 6.7 Hz), 1.40, 1.21 (2 × m, 4H), 0.86 (d, 6H, J = 6.7 Hz), 0.54 (t, 6H, J = 9.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 181.3, 139.8, 139.0, 134.1, 133.8, 131.2, 130.7, 129.4, 129.0, 42.9, 41.9, 27.1, 17.1, 17.0, 11.8, 11.4; elemental analysis calcd (%) for $C_{28}H_{33}SbO_4$ (554.8): C 60.6, H 5.9; found: C 60.2, H 5.5.

(*RR*,*SS*,*RS*)-SbPh$_3$[O$_2$CCH(Me)Ph]$_2$ (4g): Prepared by a similar procedure to that described earlier for **3g**, using **2** (76 %). IR (KBr): $\tilde{\nu}$ = 1650 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (m, 6H), 7.34 (m, 4H), 7.32 (m, 9H), 7.17 (m, 6H), 3.51 (q, 2H, ^3J = 6.9 Hz), 1.26 (d, 6H, ^3J = 6.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.1*, 133.7, 130.8, 129.0, 128.2, 127.5, 126.4, 46.8*, 18.2*; elemental analysis calcd (%) for $C_{36}H_{33}SbO_4$ (617.8): C 66.3, H 5.1; found: C 66.4, H 5.1. *Splitting observed.

(*RR*,*SS*,*RS*)-SbPh$_3$[O$_2$CCH(C$_5$H$_9$)Ph]$_2$ (4h): Prepared by a similar procedure to that described earlier for **3h**, using **2** (76 %). IR (KBr): $\tilde{\nu}$ = 1663 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, 6H, J = 9.0 Hz), 7.39 (m, 3H), 7.28 (m, 6H), 7.13 (m, 10H), 3.13 (d, 2H, J = 11 Hz), 2.37 (m, 2H), 1.55–1.30, 1.0–0.8 (2 × m, 16H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 177.0*, 139.7, 138.0, 133.6, 128.9, 130.7, 128.3, 128.0, 126.4, 59.4, 42.9, 31.2*, 30.7,

25.2, 24.9; elemental analysis calcd (%) for $C_{44}H_{45}SbO_4$ (759.6): C 69.6, H 5.9; found: C 69.4, H 5.9. *Splitting observed. Single crystals of the diastereoisomer (*RS*)-**(4h)** suitable for X-ray crystallography were grown by slow evaporation of a THF solution.

***(RR,SS,RS)*-SbPh$_3$[O$_2$CCH(OMe)Ph]$_2$ (4i)**: Prepared by a similar procedure to that described earlier for **3i**, using **2** (69%). IR (KBr): $\tilde{\nu}$ = 1653 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65 (m, 6H), 7.41 (m, 4H), 7.31 (m, 9H), 7.29 (m, 6H), 4.54* (s, 2H), 3.18, 3.19 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.0*, 138.5, 138.3, 133.6, 129.1, 128.2, 127.1, 127.0, 126.4, 83.3, 83.2, 56.8: elemental analysis calcd (%) for $C_{44}H_{45}SbO_4$ (683.4): C 63.2, H 4.9; found: C 63.1, H 4.8. *Splitting observed. Single crystals of the diastereoisomer *(RR,SS)*-**(4i)** suitable for X-ray crystallography were grown from a THF solution.

***(RR,SS,RS)*-SbPh$_3$[O$_2$CCH(OPh)Me]$_2$ (4j)**: Prepared by a similar procedure to that described earlier for **3j**, using **2** (76%). IR (KBr): $\tilde{\nu}$ = 1663 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78 (m, 6H), 7.41 (m, 9H), 7.08 (m, 4H), 6.85 (m, 2H), 6.58 (d, 4H, J = 8.0 Hz), 4.46 (q, 2H, J = 6.9 Hz), 1.32 (d, 6H, J = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.5*, 157.9*, 136.4*, 133.9, 131.2, 129.4, 129.3*, 120.8, 114.8*, 73.0, 72.9, 18.5*; elemental analysis calcd (%) for $C_{36}H_{33}SbO_6$ (682.8): C 63.3, H 4.9; found: C 63.1, H 5.0. *Splitting observed.

***(RR,SS,RS)*-SbPh$_3$[O$_2$CC(CF$_3$)(OMe)Ph]$_2$ (4k)**: Prepared by a similar procedure to that described earlier for **3k**, using **2** (71%). IR (KBr): $\tilde{\nu}$ 1675, 1312, 1259, 1122 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98 (d, 6H, J = 6.5 Hz), 7.49 (m, 9H), 7.20 (m, 2H), 7.05 (m, 8H), 3.16 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.0, 135.7*, 134.3, 133.5, 131.8, 129.5, 128.8, 127.9, 127.2, 123.7 (q, $^1J_{C,F}$ = 288 Hz), 84.3 (q, $^2J_{C,F}$ = 27 Hz), 54.8; ^{19}F NMR (235 MHz, $CDCl_3$) = −71.6, −71.7; elemental analysis calcd (%) for $C_{38}H_{31}SbO_6F_6$ (723.0): C 55.7, H 3.8; found: C 55.4, H 3.8. *Splitting observed.

Resolution study: (*R*)-Ag:**c** (0.75 g, 2.9 mmol) was added to a rapidly stirred solution of **1** (1.48 g, 2.9 mmol) in THF (40 mL). After 0.5 h, (*R*,*S*)-**c** (1.5 g, 5.81 mmol) was added and the mixture was stirred for a further 1 h. The insoluble salts were collected by filtration and washed thoroughly with THF. The solid was suspended in acetone (5 mL), cooled to −10 °C and the rapidly stirred solution acidified with conc. H_2SO_4 before being poured into Na_2CO_3 (aq). The heterogeneous mixture was extracted with $CHCl_3$ and the combined extracts dried ($MgSO_4$) and reduced in vacuo to afford a white solid characterised as 1,3-dioxolan-2,2′-dimethyl-5-phenyl-4-one (**6**).[26] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45 (m, 5H), 5.39 (s, 1H), 1.70 (d, 6H, J = 15 Hz). Gas chromatography using a chiral column afforded separation of the enantiomers accordingly (*R*)-**6** = 11.43 and (*S*)-**6** = 12.31 min (160 °C isothermal, 1.0 mL min^{-1}). The order of elution was established by the preparation of (*R*)-**6** from (*R*)-**c**.

Data retrieval: Crystal structures were located within version 5.21 (April 2001 release) of the Cambridge Structural Database (CSD) which contained 233 218 entries using the QUEST program.[27]

X-ray crystallography: *Data collection:* Data were collected at 120 K on a Bruker-Nonius KappaCCD area detector diffractometer at the window of a rotating anode FR591 generator with a molybdenum target [λ($Mo_{K\alpha}$) = 0.71073 Å] and controlled by the COLLECT[28] and DENZO[29] software packages. Data were corrected for absorption using the empirical method employed in SORTAV.[30]

Structure solution and refinement: The structures were solved by direct methods (SHELXS-97[31]) 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 (C–H distance = 0.97 Å) with isotropic displacement parameters riding on those of the parent atom. The weighting Scheme used was $w = 1/[\sigma^2(F_o^2)]$. The methoxy group of structure **4i** is disordered over two positions, with the major component (83% occupied) being depicted in Figure 2. See Table 3 for structural data.

CCDC-194654 (**4h**) and -194655 (**4i**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; (fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

Table 3. Crystal data for **4h** and **4i**.

	4h	**4i**
empirical formula	$C_{44}H_{45}O_4Sb$	$C_{36}H_{33}O_6Sb$
formula weight	759.55	683.37
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$
a [Å]	9.540(2)	17.004(3)
b [Å]	13.248(3)	9.741(2)
c [Å]	28.592(6)	18.658(4)
β [°]	98.73(3)	102.59(3)
V [Å^3]	3571.6(12)	3016.0(10)
Z	4	4
ρ_{calcd} [mg m^{-3}]	1.413	1.505
abs. coeff. [mm^{-1}]	0.816	0.961
F(000)	1568	1392
crystal size [mm]	0.15 × 0.15 × 0.1	0.18 × 0.16 × 0.04
θ_{max} [°]	27.50	27.48
refls coll.	57917	13486
indep. refls	7391	3446
R(int)	0.0723	0.0440
final R indices $F^2 > 2\sigma F^2$		
$R1$	0.0778	0.0276
$wR2$	0.1866	0.0630
$\Delta\rho$ max/min [e Å^{-3}]	1.434/−1.477	0.707/−0.709

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