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Synthesis and structure of organoantimony (V) cyclometallates: transannular interactions and the barrier to cyclisation

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Abstract

A variety of α-hydroxy carboxylic acid salts $[AgO_2CC(OH)R^1R^2]$ react with $SbPh_3Cl_2$ **1** to afford the cyclometalled complexes **4b–g**. A single crystal X-ray analysis of (±)-**4g** reveals the presence of conformational diastereoisomers arising from the helical chirality of the $SbPh_3$ propeller unit. Benzilic acid ($R^1 = R^2 = Ph$) however, reacts with **1** to afford the di-ester **3**. To rationalise the steric impediment to cyclisation, the solid-state geometries of all known five coordinate dioxo cyclometallates possessing an integral XPh_3 unit are presented, along with the accessible conformations for each structural alternative. Computer modelling and crystallographic correlations identify severe 1,3-transannular interactions within the fluxional species associated with the nascent cyclometallate of benzilic acid. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cyclometallation; Antimony; 1,3-Transannular interactions

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1. Introduction

Five coordinate structures have received much attention because of the important role they play in the mechanisms of associative reactions of four coordinate phosphorus species [1]. The preferred geometry of five coordinate Group 15 elements [2] is the trigonal-bipyramid (TBPY) which is a fluxional, stereochemically non-rigid or pseudorotating [3] arrangement rapidly interconverting with the alternative square-pyramid (SP) structure. The energy difference between the two structural alternatives is small both in solution [4] and the solid state, where the nature of the counterion for charged species, lattice effects and the solvent of crystallisation play a determining role [5]. The delicate balance between the two structural alternatives may be illustrated [6] by the fact that $AsPh_5$, $Sb(tol)_5$ [7], and cyclohexane solvates of $MPh_5{:}0.5C_6H_{12}$ (M = Sb or As) adopt the TBPY geometry in the solid-state, whereas MPh_5 (M = Sb or Bi) adopts the alternative SP arrangement. An appreciation of the pseudorotational processes occurring during the lifetime of a five-coordinate intermediate is clearly important for predicting and ultimately controlling product stereochemistry. We present here the contrasting reactivity of α-hydroxy carboxylates with $SbPh_3Cl_2$ **1**. As a contribution towards understanding the stereochemistry of nucleophilic substitution at tetrahedral Group V centres [8], the solid-state geometries of all known five coordinate dioxo cyclometallates possessing an integral XPh_3 unit are presented. In addition, the accessible conformations for each structural alternative have been identified using a combined X-ray crystal structure/computational approach, thereby extending our current understanding

Table 1
α-Hydroxy carboxylic acids **a**–**g** $[HO_2C\text{–}C(OH)R^1R^2]$

Acid	R^1	R^2
a	Ph	Ph
b	H	Ph
c	H	p-$CF_3C_6H_4$
d	H	p-$MeOC_6H_4$
e	H	Me
f	H	Et
g	Me	Et

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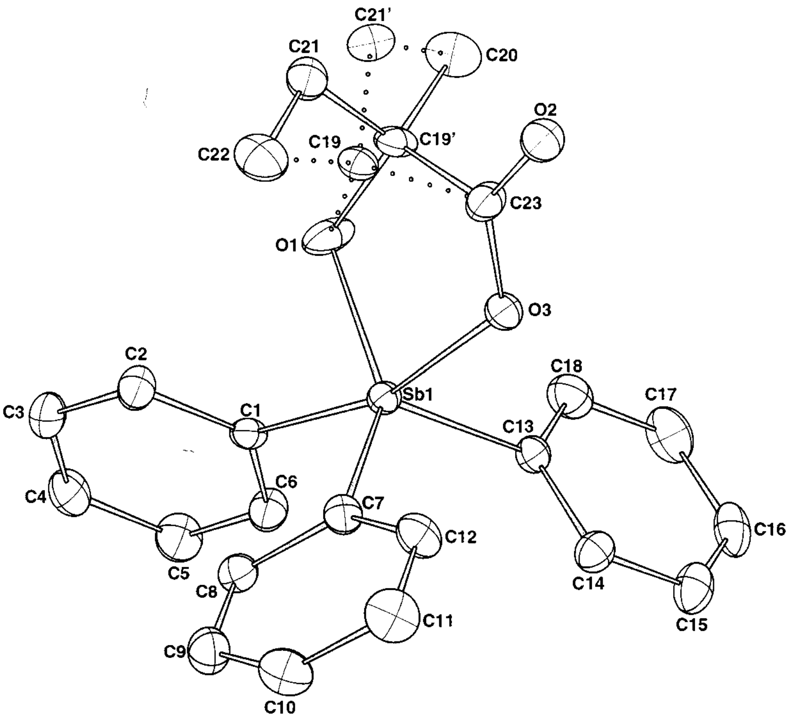


Fig. 1. The X-ray crystal structure of the conformational diastereoisomers (*SR*,PM)-**4g** and (*RS*,PM)-**4g**. Using the P propeller configuration as the frame of reference, the major (*S*) and minor (*R*) diastereoisomers are represented in bold and dashed lines, respectively.

of propeller systems [9,10] to TBPY↔SP pseudorotation processes.

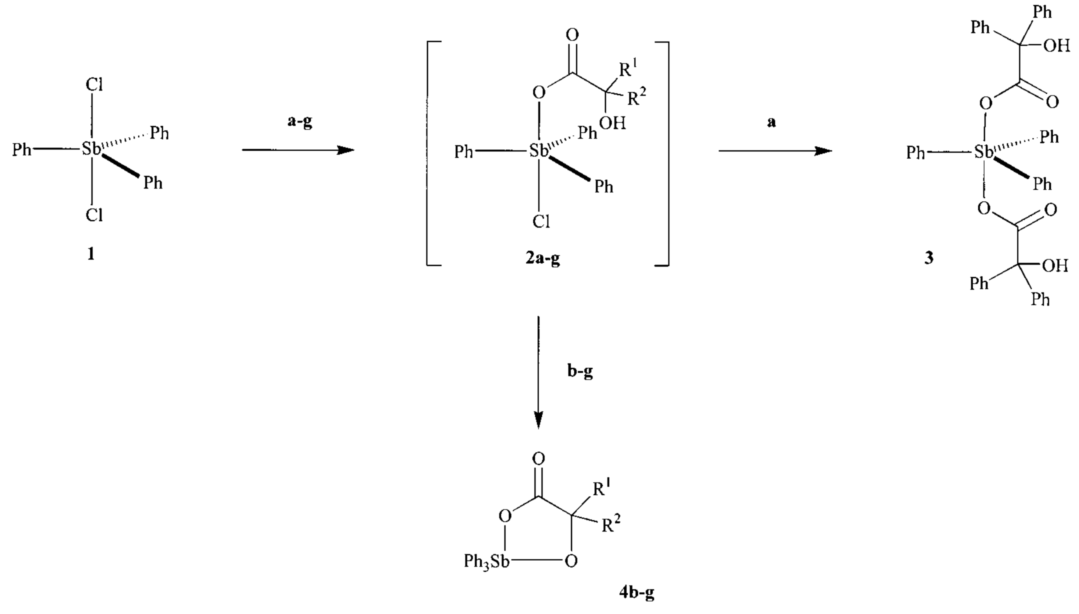
2. Results

Triaryl antimony di-carboxy esters of the type $SbAr_3(O_2CR)_2$ may be prepared by the metathetical reaction of the dihalide $SbAr_3X_2$ (X = Br or Cl) with the corresponding carboxylate anion [11]. For example, a stirred THF solution of $SbPh_3Cl_2$ (**1**) and two equivalents of the silver salt of benzilic acid (**a**, Table 1) affords the di-ester **3** in high yield (Scheme 1) [12]. In contrast, **1** reacts with two equivalents of the silver salt of (±)-mandelic acid (**b**, Table 1) to afford the cyclometallate (±)-**4b** ($R^1/R^2 = H/Ph$, Scheme 1), also in high yield. Here, formation of **4b** is accompanied by one equivalent of both AgCl and HCl; the latter presumably 'quenches' unreacted Ag:**b** thereby liberating the free acid. In order to examine whether **4b** reacts with an excess of Ag:**b**, a 1:1 mixture of the two was stirred in THF for 24 h without change. Stirring **1** in the presence of three equivalents of Ag:**b** affords the cyclometallate **4b** alone, as established by ^{1}H-NMR analysis of the crude reaction mixture. The complex **4b** may also be prepared directly using one equivalent of Ag:**b**. It is concluded therefore that under the reaction conditions employed, cyclometallate **4b** is not an isolated intermediate en route to the corresponding di-ester.

The molecular structure of **4g** is presented in Fig. 1 together with the atomic numbering scheme, whilst selected bond lengths and angles are presented in Table 2. The complex is composed of an antimony metal centre coordinated to three phenyl ligands and the bidentate $O_2CC(O)(Me)Et$ moiety. When considering the geometry of five coordinate structures one must use the Berry formalism [3], which graphically describes the change in the sum of dihedral angles between coordina-

Table 2
Selected bond lengths (Å) and angles (°) for **4g**

Bond lengths			
Sb(1)–O(1)	1.936(4)	Sb(1)–O(3)	2.133(3)
Sb(1)–C(1)	2.138(5)	Sb(1)–C(7)	2.112(4)
Sb(1)–C(13)	2.115(4)	O(3)–C(23)	1.286(6)
O(1)–C(19)	1.567(12)	O(1)–C(19′)	1.437(8)
C(23)–C(19)	1.562(12)	C(23)–C(19′)	1.611(10)
C(19)–C(22)	1.634(11)	C(19′)–C(20)	1.586(13)
C(19)–C(21′)	1.542(12)	C(19′)–C(22)	1.533(12)
C(21′)–C(20)	1.449(11)	C(21)–C(22)	1.469(10)
Bond angles			
O(1)–Sb(1)–C(1)	101.81	O(1)–Sb(1)–C(7)	121.60(15)
O(1)–Sb(1)–C(13)	123.33(15)	O(1)–Sb(1)–O(3)	77.75(14)
O(3)–Sb(1)–C(1)	163.67(17)	O(3)–Sb(1)–C(7)	88.84(13)
O(3)–Sb(1)–C(13)	85.55(13)	C(1)–Sb(1)–C(7)	101.67(14)
C(1)–Sb(1)–C(13)	101.81(14)	C(7)–Sb(1)–C(13)	111.59(17)



Scheme 1.

tion faces on transforming from idealised TBPY to SP geometries. The arrangement of **4g** is 24.1% along the Berry pseudorotation coordinate, indicating a molecular geometry more similar to TBPY than SP. However this geometry is 22.4° off the Berry coordinate which suggests that this complex does not undergo a true Berry rotation. This indicates that when proceeding from TBPY to a SP arrangement via the turnstile mechanism [15], the constraints upon the fluxional geometry imposed by the chelating ligand cause considerable distortion between the faces of the coordination polyhedra, producing a solid state structure geometry that is somewhat deformed from ideal values. The complex (±)-**4g** crystallises as two conformational diastereoisomers by virtue of the propeller, or helical chirality of the correlated propeller unit [13]. The diastereoisomerism gives rise to disorder at the apex of the chelate ring. The conformational diastereoisomer (*SR*,PM)-**4g** exhibits 60% occupation, whilst (*RS*,PM)-**4g** comprises 40% of the crystal composition [14]. Single point energy calculations[1] upon the optimised structures indicate a small preference (<2 kJ mol^{-1}) for (*SR*,PM)-**4g**.

Assuming that the Cl ligands in **1** are displaced in a stepwise fashion, it follows that di-ester **3** and cyclometallate **4b** share a common intermediate, namely mono-ester **2** (Scheme 1)[2]. The rate at which **2** undergoes subsequent cyclometallation to afford **4** is presumably governed by steric and/or electronic factors. To probe whether the selectivity exhibited by Ag:**a**/**b** towards **1** is influenced by small changes in the pK_a of the α-hydroxy group, the reaction of **1** with the *para* CF_3 and OMe analogues of (±)-mandelic acid (**c** and **d**, respectively, Table 1) were examined; the corresponding metallocycles **4c**–**d** (Scheme 1) were formed exclusively. The reaction of **1** with the silver and sodium salts of several chiral aliphatic hydroxy acids possessing varying degrees of steric congestion at the α-position were subsequently examined (**e**–**g**, Table 1). The corresponding metallocycles (±)-**4e**–**g** were recovered in high yields. β-Hydroxy carboxylic anions, such as those derived from salicylic [12] and 2-hydroxybutyric acids failed to form cyclic complexes with **1**, affording the alternative di-esters. These observations indicate that prohibitive steric and/or geometrical factors attend the attempted cyclisation of **2a** ($R^1 = R^2 =$ Ph).

3. Discussion

3.1. Characterising complex geometries and accessible conformations

To characterise the steric impediment to the cyclisation of **2a**, accessible complex geometries on the pathway **2**→**4** are considered here. A search of the CSD for five coordinate systems analogous to **4**, possessing an integral triphenyl unit XPh_3 (X = central atom) and a bidendate dioxo chelating ligand revealed examples of both SP and TBPY arrangements (**4**-SP and **4**-TBPY, Fig. 2). The interconversion **4**-SP↔**4**-TBPY can be

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[1] Hartree-Fock at the 3-21G(*) level using PC Spartan Pro (1.0.3). Designed and distributed by Wavefunction Inc., 18401 Von Karman, Suite 370, Irvine CA 92612, USA.

[2] H-NMR analysis ($CDCl_3$) of a heterogeneous mixture of **1** and Ag:**e** for example, reveals the formation of both **2e** [δ: 8.07 (m, *o*-Ph),

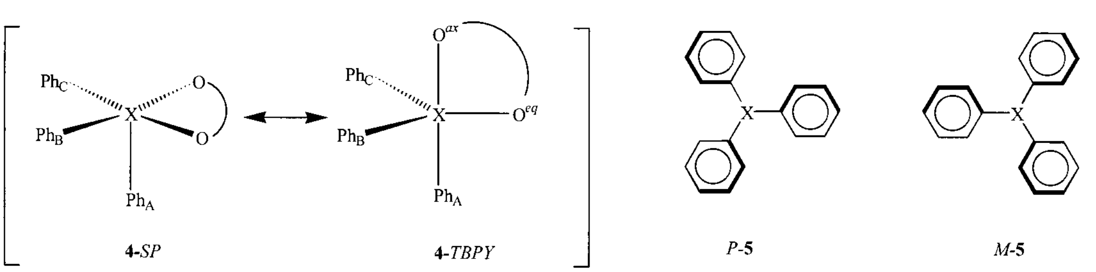


Fig. 2. Alternative SP and TBPY structural arrangements of **4** and the preferred enantiomeric P and M propeller arrangements of a correlated XPh_3 system **5**.

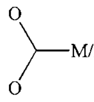
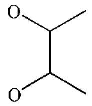
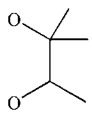
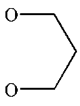
envisaged as free spinning of the bidendate ligand above the triangular array of Ph ligands (i.e. the turnstile mechanism of pseudorotation) [15]. Distorted structures [16] of the type **4**-SP possessing four (X = Sb [17]), five (X = P [18], Sb [19], Sn [20]) and six (X = Te [21]) membered dioxo chelates invariably adopt an arrangement where the bidendate dioxo moiety spans the basal edge (Fig. 2). The dioxo moiety of **4**-TBPY invariably spans axial and equatorial sites (Fig. 2 and Table 3 [22a–n]).

When two or more aryl rings are bonded to a central atom X (i.e. CPh_2 in benzilic acid, or XPh_3 in **4**-SP/TBPY, Fig. 2) rotation about a given X–C_i bond is coupled in the sense that no ring moves independently of the other [23]. Aryl rings within such systems minimise steric inter ring–ring interactions by twisting about the X–C_i bond in the same sense, affording a correlated arrangement. The vector perpendicular to the plane defined by all three C_i atoms (the reference plane) and incident upon X is recognised as an axis of chirality described in terms of two enantiomeric propeller configurations, i.e. clockwise (**P-5**) and anticlockwise (**M-5**), respectively (Fig. 2).

Molecular modelling studies using the CHEM-X* package (which employs electrostatic and van der Waals interaction energy calculations upon structures generated by simple rigid rotations) have been used to examine the preferences of the XPh_3 unit in **4**-SP and **4**-TBPY. A model of **4**-SP based upon $SbPh_3(OH)_2$ [24] was constructed using average bond lengths derived from the crystallographic data of triphenylantimony catecholate [19a]. The Newman projection (viewed along the basal plane) of the resultant minimum energy arrangement of **4**-SP (**I** Fig. 3: $E = 0$ kJ mol^{-1}) is attended by all-*gauche* inter ring-ligand orientations. The alternative chiral structure **II** is destabilised by Ph_{A-B}/O atom interactions ($E = +17$ kJ mol^{-1}). The calculated minimum energy arrangement **I** resembles the solid-state structure of X = P [18], while **II** resembles the crystal structure of X = Te [21]. Structures where X = Sn/Sb possess residual TBPY character and do not provide a useful comparison.

A model of **4**-TBPY based upon $SbPh_3(OH)_2$ was constructed using appropriate bond lengths and angles derived from the crystal structure of triphenyltrioxastibolane [22m]. The thermodynamically preferred conformation was calculated in precisely the same manner described above for **4**-SP. A Newman projection (viewed perpendicularly with respect to the reference plane) of the calculated lowest energy arrangement **III** (Fig. 4) demonstrates a clear preference for a non-correlated arrangement. Chiral **IV** is destabilised with respect to **III** by inter ring/O atom interactions

Table 3
Crystallographic data [22] associated with complexes of the form **4**-TBPY [a]

Bidendate ligand		IV	V
A		JIDLUD[a] (Sn) FODLAL[b] (Sn) NOMQIP[c] (Sn) YEGCUI[d] (Sn) HAMSAP[e] (Sn) YOTBOY[f] (Sn)	HADNUV[h] (Sn) KUVVEC[i] (Sn) DUGFEQ[j] (Sb)
B		RABZOJ[g] (Sn)	FAZSUU[k] (Sb) TPSNBH10[l] (Sn)
C		**4g** (Sb)	DUGFIU[m] (Sb)
D		PPTPSN[n] (Sn)	

[a] M = Fe or Re, and R = organic fragment.

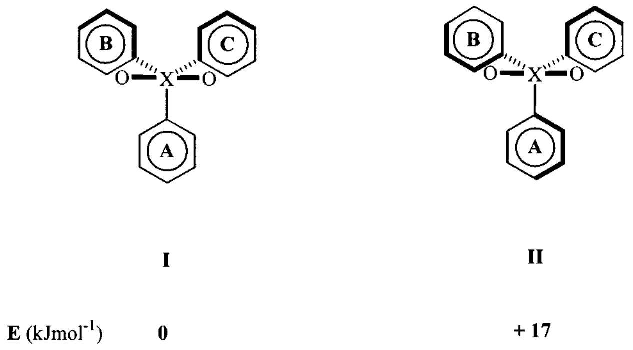


Fig. 3. Achiral (**I**) and chiral (**II**) arrangements of **4**-SP. The H atoms associated with the OH ligands have been omitted for clarity.

($\Delta E = +8$ kJ mol^{-1}). All complexes in the CSD of the form **4**-TBPY are presented in Table 3. Chelates are classified according to the atom type (X = Sb/Sn), ring size and degree of unsaturation within the ring (i.e., **A**: $1 \times sp^2$; **B**: $2 \times sp^2$, **C**: $1 \times sp^2/sp^3$, and **D**: $3 \times sp^2$). Conformations corresponding to the calculated lowest energy arrangement **III** were not observed in the solid-state. Several examples of chiral **IV** were, in addition to **V** ($\Delta E_{V-III} = +21$ kJ mol^{-1}, Fig. 4) which resembles the transition-state for the one ring-flip stereoisomerisation process. Assuming that the conformations adopted in the solid-state represent favoured arrangements on the potential energy surface of a complex, the occurrence of **IV** and **V** indicate a low energy stereoisomerisation pathway for chiral **IV** [(M)↔(P)] via the achiral structure **V**. The latter serves as an intermediate rather than a transition-state [25]. In conclusion, **I**/**II** and **IV**/**V** are observed in the solid-state, whereas **III** is not. It is unwise to speculate upon the free energy in solution of given arrangements and their popularity in the CSD. Nevertheless, as **I**–**V** are thermodynamically accessible five coordinate species it must be assumed that they will contribute towards the net reaction rate of cyclisation.

3.2. 1,3-Transannular interactions and cyclisation

Attention turns to the 1,3-transannular interactions involving $XPh_{2\text{-}3}$ units in five membered chelates. Newman projections (viewed along the C_α/Sb axis, Fig. 5(a–b)) of the conformational diastereoisomers (*S*,P)-**4g** and (*R*,P)-**4g** illustrate that chiral arrangement **IV** adopted by the $SbPh_3$ unit. For (*S*,P)-**4g** (Fig. 5(a)), transannular 1,3-interactions are minimised as the smallest substituent (i.e. CH_3) and is oriented towards the apex of ring **B**. Conversely, the epimeric structure i.e. (*R*,P)-**4g** (Fig. 5(b)) presents the larger CH_2CH_3 substituent towards the apex of ring **B**. This clashing interaction is accommodated by a twisting of the five-membered chelate from a near planar to a C_s or envelope arrangement [Δ(*R*,P)-(*S*,P) O–C–C_α–O = 23°]. It is clear that clashing 1,3 transannular interactions may be accommodated via ring puckering, in the ground state at least [26].

The solid-state conformations adopted by bimetallic complexes of bis(diphenylphosphino)methane (dppm) [i.e. $M_2(PPh_2CH_2PPh_2)$ **5**, Fig. 6] reveal a strong coupling between 1,3-disposed phenyl groups [27]. As anticipated, the geminal phenyl rings adopt a mutually orthogonal arrangement [28]. The five-membered M_2P_2C ring constrains the relative orientation of the pseudo-axial 1,3-disposed phenyl groups to adopt a face-on arrangement. Transannular gearing follows as the geminal units transmit a complementary edge-on orientation of the pseudo-equatorial phenyl groups, as depicted in **5** (Fig. 6).

The CSD was examined for examples of five-membered rings containing 1,3-disposed $XPh_{2\text{-}3}$ units as models for the cyclisation of **2a** (Scheme 1). One example was found to possess the structural features outlined above, namely $1\lambda^5,3\lambda^5$-benzodiphosphole **6** (Fig. 7) [29]. The geometry about the PPh_3 unit in **6** is TBPY, and the rings of the PPh_2 unit are mutually orthogonal. The rings of the PPh_3 unit adopt the arrangement predicted by calculation i.e. **III** (Fig. 4). Importantly, the 1,3-transannular gearing observed in M_2P_2C ring systems

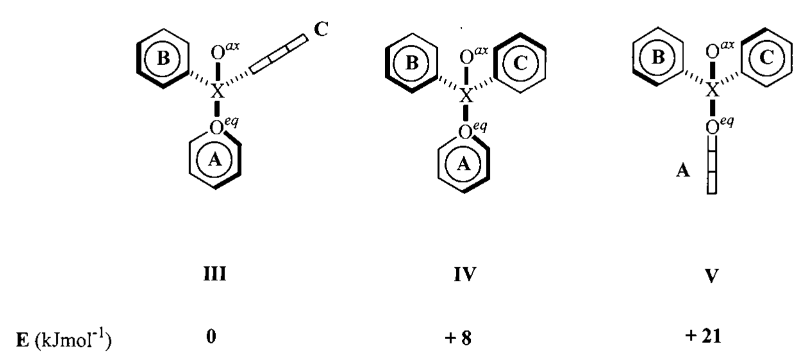


Fig. 4. Calculated achiral (**III**, **V**) and chiral (**IV**) arrangements of **4**-TBPY. The H atoms associated with the OH ligands have been omitted for clarity.

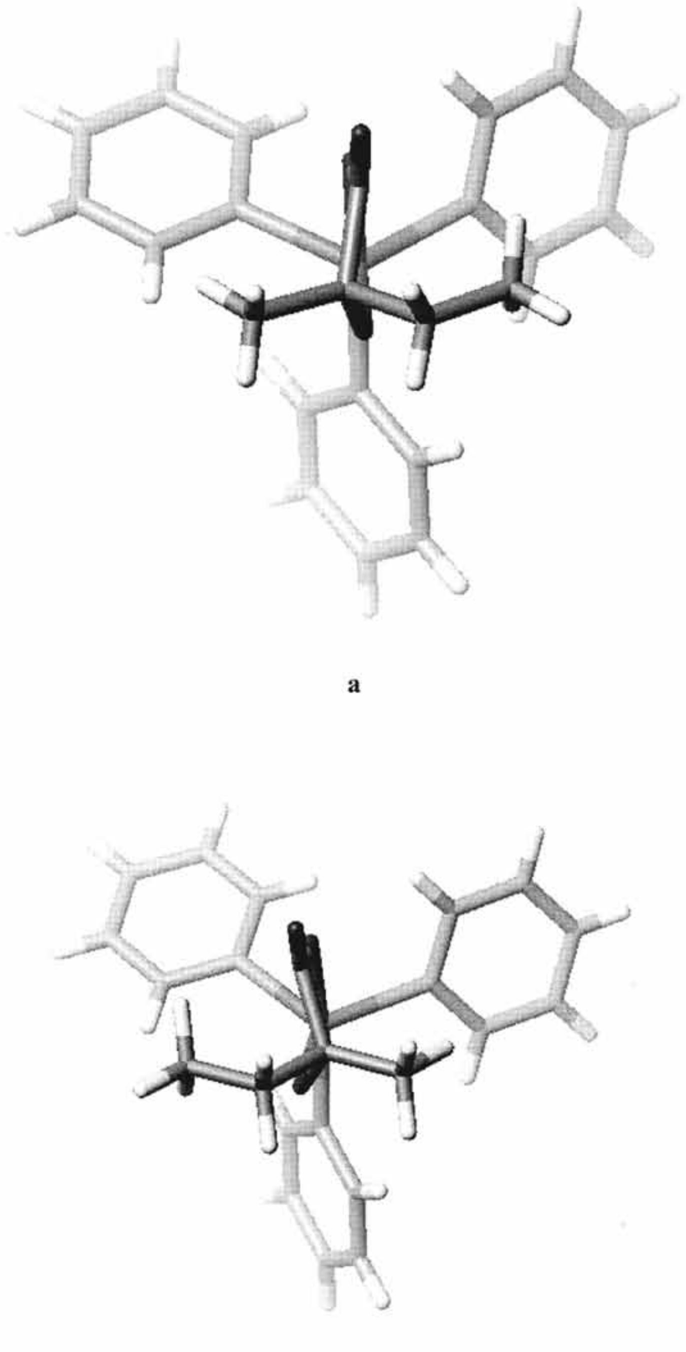


Fig. 5. Conformational diastereoisomers (a) (*S*,P)-**4g** and (b) (*R*,P)-**4g**.

(i.e. **5**) is observed in **6** (Newman projection **7**, Fig. 7). The edge-on orientation of Ph_C is accommodated by a staggered arrangement of the synclinal ring of the PPh_2 unit. A face-on arrangement involving Ph_B and the corresponding synclinal ring of the PPh_2 unit appears to be energetically acceptable. In conclusion, X-ray crystal structure correllations suggest a preference for face/edge-on meshing in five-membered chelates possessing 1,3-disposed XPh_3/XPh_2 units.

The SP nascent cyclometallate of **4a** is presented in Fig. 7 (Newman projection viewed approximately along the C_α…Sb axis). Conformation **I** alone may accommodate the preferred face-on arrangement of the XPh_3 (ring **A**) and XPh_2 units. However, ring **B** of the XPh_3

unit adopts a destabilising 1,3-edge-face interaction with the XPh_2 moiety. It may be concluded therefore that cyclometallation of **2a** via a SP transition structure will attenuate the overall rate of reaction because of clearly identifiable transannular Ph/Ph clashing interactions. The thermodynamically accessible conformers of the TBPY structural alternative are presented in Fig. 7. Conformer **III** (resembling **6**) presents itself as a low energy pathway for the cyclisation of **2a** as it possesses complementary face/edge-on interactions. Conformers **IV**–**V** however, possess non-complementary face/edge-on arrangements of the XPh_3 (ring **B**) and XPh_2 units.

In conclusion, X-ray crystallographic correlations and conformational analyses suggest that SP **I**–**II** and TBPY **III**–**IV** (which racemises via **V**) arrangements contribute towards the structure of five coordinate **4**. In the case of **2a**, the formation of sterically strained arrangements derived from **I**–**II** and **IV** attenuate the net rate of cyclisation in solution to the extent that this is not observed.

4. Experimental

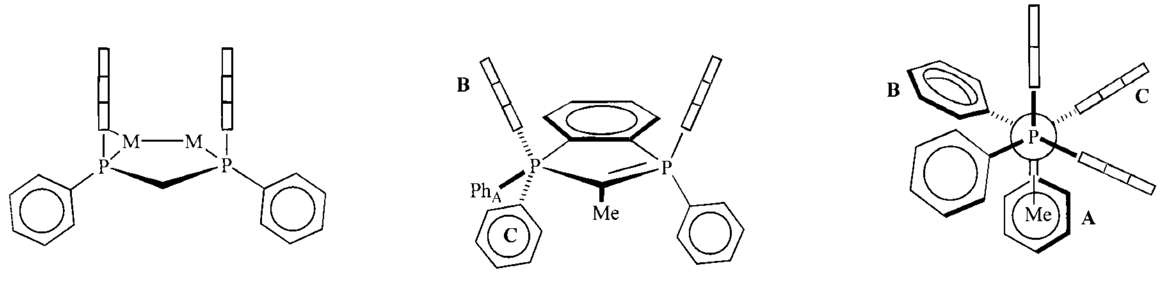
4.1. General procedures

All reactions were performed under an atmosphere of dry nitrogen. Tetrahydrofuran (THF) was distilled under an atmosphere of nitrogen from sodium benzophenone ketyl. 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 salt by reaction with $AgNO_3$. ^1H-NMR spectra were recorded on either a Jeol EX 270 (270 MHz), or an Eclipse + 400 (400 MHz) spectrometer, using $CDCl_3$ as solvent and referenced to residual $CHCl_3$, with chemical shifts being reported at δ (ppm) from tetramethylsilane and J values measured in Hz. ^{13}C-NMR (DEPT) spectra were recorded on either a Jeol 270 or 400 MHz spectrometer operating at 68 and 100 MHz, respectively, using $CDCl_3$ as solvent and reference (77.0 ppm). ^1H and ^{13}C nuclei corresponding to C_6H_5 groups associated with the carboxylate 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.

4.2. Preparations

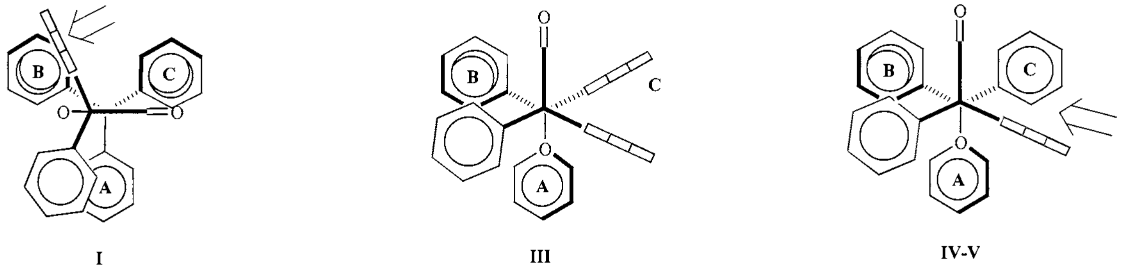
4.2.1. (RS)-$SbPh_3O_2CCH(O)Ph$ (**4b**)

The silver salt of (*RS*)-$HO_2CCH(OH)Ph$ **b** (610 mg, 2.35 mmol) was added to a solution of $SbPh_3Cl_2$ (500 mg, 2.35 mmol) in THF (10 ml) and stirred at room temperature (r.t.) for ca. 12 h in the absence of light. After filtration, a clear solution was obtained which was concentrated in vacuo (ca. 2–3 ml). After the addition of hexane (5 ml), the solution was allowed to stand overnight at 0°C affording a white crystalline solid characterised as **4b** (71%). Anal. Calc. for $C_{26}H_{21}SbO_3$: C, 62.0; H, 4.2. Found: C, 62.0; H, 4.1%. IR [KBr, ν cm^{-1}]: 1593 (C=O). ^1H-NMR (270 MHz, $CDCl_3$, 298 K): 7.75 m (*o*-Ph), 7.45 m (*m*, *p*-Ph, *o*-Ph′), 7.21 m (*m*, *p*-Ph′), 5.39 s (H_α). ^{13}C-NMR (68 MHz, $CDCl_3$, 298 K): 174.3 (C=O), 139.8 (*i*-C′), 135.6, 129.7



5 **6** **7**

Fig. 6. Transannular gearing of the phenyl rings in bimetallic complexes of the type $M_2(PPh_2CH_2PPh_2)$ **5**. A complementary representation of the solid-state structure of benzodiphosphole **6**, with Newman projection **7** (viewed along the $Ph_2P...PPh_3$ axis).



I **III** **IV-V**

Fig. 7. Transannular interactions attending the cyclometallation of **2a**. Newman projections viewed along the $C_\alpha...Sb$ axis.

(*o*, *m*-C), 135.0 (*i*-C), 131.9 (*p*-C), 128.4, 126.6 (*o*, *m*-C′), 127.6 (*p*-C′),73.7 (C_α).

4.2.2. *(RS)-$SbPh_3O_2CCH(O)p$-$CF_3C_6H_4$* **(4c)**

Compound **4c** was prepared using a similar procedure with the silver salt of (*RS*)-**c** (73%). Anal. Calc. for $C_{27}H_{20}F_3SbO_3$: C, 56.7; H, 3.5. Found: C, 56.5; H, 3.5%. IR [KBr, ν cm^{-1}]: 1598 (C=O), 1325 (C–F). ^{1}H-NMR (400 MHz, $CDCl_3$, 298 K): 7.75 m (*o*-Ph), 7.50 m (*o*, *m*-Ph′), 7.48 m (*m*, *p*-Ph), 5.39 s (H_α). ^{13}C-NMR (100 MHz, $CDCl_3$, 298 K): 173.4 (C=O), 135.4, 129.6 (*o*, *m*-C), 134.6 (*i*-C), 132.1 (*p*-C), 126.6 (*o*, *m*-C′), 125.1 (q, CF_3), 73.1 (C_α).

4.2.3. *(RS)-$SbPh_3O_2CCH(O)p$-$MeOC_6H_4$* **(4d)**

Compound **4d** was prepared using a similar procedure with the silver salt of (*RS*)-**d** (73%). Anal. Calc. for $C_{27}H_{23}SbO_4$: C, 60.8; H, 4.5. Found: C, 60.6; H, 4.4%. IR [KBr, ν cm^{-1}]: 1595 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$, 298 K): 7.76 m (*o*-Ph), 7.52 m (*m*, *p*-Ph, *o*-Ph′), 7.42 m (*m*-Ph′), 5.32 s (H_α), 3.78 s (OCH_3). ^{13}C-NMR (100 MHz, $CDCl_3$, 298 K): 174.6 (C=O), 135.4, 131.8 (*o*, *m*-C), 134.9 (*i*-C), 132.0 (*p*-C), 129.5 (*o*-C′), 127.7 (*m*-C′), 76.6 (C_α), 53.1 (OCH_3).

4.2.4. *(RS)-$SbPh_3O_2CCH(O)Me$* **(4e)**

Compound **4e** was prepared using a similar procedure with the silver salt of (*RS*)-**e** (86%). Anal. Calc. for $C_{21}H_{19}SbO_3$: C, 57.1; H, 4.3. Found: C, 57.5; H, 4.7%. IR [KBr, ν cm^{-1}]: 1597 (C=O). ^{1}H-NMR (270 MHz, $CDCl_3$, 298 K): 7.71 m (*o*-Ph), 7.51 m (*m*, *p*-Ph), 4.48 q, $^{3}J_{HH} = 6.6$ Hz (CH), 1.43 d, $^{3}J_{HH} = 6.6$ Hz (CH_3). ^{13}C-NMR (68 MHz, $CDCl_3$, 298 K): 177.3 (C=O), 135.3, 129.4 (*o*, *m*-C), 135.0 (*i*-C), 131.8 (*p*-C), 68.3 (C_α), 21.4 (CH_3).

4.2.5. (*RS*)-$SbPh_3O_2CCH(O)Et$ *(***4f***)*

Compound **4f** was prepared using a similar procedure with the silver salt of (*RS*)-**f** (76%). Anal. Calc. for $C_{22}H_{21}SbO_3$: C, 58.0; H, 4.6. Found: C, 57.9; H, 4.6%. IR [KBr, ν cm^{-1}]: 1600 (C=O). ^{1}H-NMR (270 MHz, $CDCl_3$, 298K): 7.75 m (*o*-Ph), 7.51 m (*m*, *p*-Ph), 4.36 dd, $^{3}J_{HH} = 7.0$ Hz (H_α), 1.97 and 1.68 m (CH_2), 0.95 t, $^{3}J_{HH} = 7.3$ Hz (CH_3). ^{13}C-NMR (68 MHz, $CDCl_3$, 298 K): 176.6 (C=O), 135.4, 129.4 (*o*, *m*-C), 135.1 (*i*-C), 131.8 (*p*-C), 72.8 (C_α), 28.1 (CH_2), 9.7 (CH_3).

4.2.6. *(RS)-$SbPh_3O_2CC(O)(Me)Et$]* **(4g)**

Compound **4g** was prepared using a similar procedure with the silver salt of (*RS*)-**g** (72%). Anal. Calc. for $C_{23}H_{23}SbO_3$: C, 58.8; H, 4.9. Found: C, 58.5; H, 4.9%. IR [KBr, ν cm^{-1}]: 1680 (C=O). ^{1}H-NMR (270 MHz, $CDCl_3$, 298 K): 7.74 m (*o*-Ph), 7.50 m (*m*, *p*-Ph), 1.94 and 1.77 m (CH_2), 1.44 s (CH_3), 0.83 t, $^{3}J_{HH} = 7.4$ Hz (CH_3CH_2). ^{13}C-NMR (68 MHz, $CDCl_3$, 298 K): 179.4 (C=O), 135.4, 129.4 (*o*, *m*-C), 135.1 (*i*-C), 131.7 (*p*-C), 77.5 (C_α), 33.2 (CH_2), 26.8 (CH_3C_α), 8.7 (CH_3CH_2). Single crystals of **4g** suitable for X-ray crystal structure analysis were grown by slow evaporation of a concentrated $CHCl_3$ solution.

4.3. *Data retrieval and molecular modelling*

Crystal structures containing appropriate molecular fragments were located within the Cambridge Structural Database (CSD) [30] using the QUEST program. Data for these molecular structures were retrieved from the April 2000 release of the CSD in which the master data file contained 215 403 entries.

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 calculation, which is a subset of the full molecular mechanics suite within CHEM-X, is described elsewhere [12]. The thermodynamically preferred conformation of each structure was determined in the following manner. The torsion angles C_o–C_i–X–O for rings **A**–**C** were simultaneously driven through the range $0 \rightarrow 180°$ in 10° increments. At each point, the total van der Waals interaction energy was allowed to minimise via independent rotations about all X–C_i bonds until the default energy convergence criteria was achieved.

4.4. *Structural characterisation of* **4g**

$C_{23}H_{23}O_3Sb$, $M_r = 496.16$, monoclinic, space group $P2_1/c$, $a = 8.599(2)$, $b = 12.313(2)$, $c = 19.502(4)$ Å, $\beta = 96.77(3)°$, $U = 2050.5(7)$ Å^3, $T = 150(2)$ K, $Z = 4$, $\mu(\text{Mo}-K_\alpha) = 1.365$ mm^{-1}, $F(000) = 944$, 31702 reflections were collected, θ range 1.96–26.34° (index ranges; $h = -10$ to 10, $k = -15$ to 15 and $l = -24$ to 24), which merged to give 4173 unique reflections ($R_{int} = 0.1169$) to refine against 266 parameters. Final R indices were $wR_2 = 0.1394$ and $R_1 = 0.0441$ [$I > 2\sigma(I)$] and 0.1492 and 0.0545, respectively for all data. Residual electron densities were 1.102 and -1.589 e Å^{-3}. Data were collected using a crystal of size 0.25 × 0.20 × 0.20 mm on a Nonius KappaCCD area detector diffractometer at the window of a rotating anode FR591 generator (50 kV, 20 mA), with a molybdenum target [$\lambda(\text{Mo}-k_\alpha) = 0.71069$ Å] and controlled by the COLLECT [31] software package. Images of 2° thickness and 10 s exposure were taken for a combined π and ω scan strategy, with a detector to crystal distance of 30 mm (θ offsets between 3.3 and 9.95°) and processed by Denzo [32]. Data were corrected for absorption using the empirical method employed in Sortav [33] from within the MAXUS [34] suite of programs. The structure was solved by direct methods (SHELXS-97 [35]) and then subjected to full-matrix least squares refinement based on F_o^2 (SHELXL-97 [35]). Non hydrogen atoms were refined anisotropically with hydrogens included in idealised positions (C–H distance = 0.97 Å) with thermal parameters riding on those of the parent atom. The weighting scheme used was $w = 1/[\sigma^2(F_o^2)]$.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 150 789 for compound **4g**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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