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COVER ARTICLE

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Organoantimony(III) compounds containing (imino)aryl ligands of the type 2-(RN=CH)C_6H_4 (R = 2′,4′,6′-$Me_3C_6H_2$, 2′,6′-$^iPr_2C_6H_3$): bromides and chalcogenides†

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The reaction of 2-(RN=CH)C_6H_4MgBr [R = 2′,4′,6′-$Me_3C_6H_2$ (R^1), 2′,6′-$^iPr_2C_6H_3$ (R^2)] [prepared from 2-(R^1N=CH)C_6H_4Br (**1**) or 2-(R^2N=CH)C_6H_4Br (**2**) and Mg] with $SbCl_3$ in a 2 : 1 and 1 : 1 molar ratio followed by treatment with an aqueous KBr solution gave [2-(R^1N=CH)$C_6H_4]_2SbBr$ (**3**) and [2-(R^2N=CH)-$C_6H_4]_2SbBr$ (**4**) as well as [2-(R^1N=CH)$C_6H_4]SbBr_2$ (**6**) and [2-(R^2N=CH)$C_6H_4]SbBr_2$ (**7**). Treatment of **4** with $Na_2S{\cdot}9H_2O$ provided the dinuclear [{2-(R^2N=CH)$C_6H_4}_2Sb]_2S$ (**5**). Heterocyclic species, *i.e.* the oxide *cyclo*-[{2-(R^2N=CH)$C_6H_4}SbO]_3$ (**8**) and the sulfides *cyclo*-[{2-(R^1N=CH)$C_6H_4}SbS]_2$ (**9**) and *cyclo*-[{2-(R^2N=CH)$C_6H_4}SbS]_2$ (**10**), were obtained by reacting dibromides **6** and **7** with KOH and $Na_2S{\cdot}9H_2O$, respectively, in a water–toluene solvent mixture. The sulfide **10** reacted with [W(CO)$_5$(thf)] to yield the heterometallic complex *cyclo*-[{2-(R^2N=CH)$C_6H_4}SbS]_2[W(CO)_5]$ (**11**). The compounds were characterised by multinuclear NMR spectroscopy in solution, mass spectrometry and IR spectroscopy in the solid state. The molecular structures of **4**, **5**, **6**·$CHCl_3$, **7**, **9**·CH_2Cl_2, **10** and **11**·0.25CH_3OH were established by single-crystal X-ray diffraction. Theoretical calculations using DFT methods were carried out on bromide **7** and the geometrical isomers of its dimer association as well as the geometrical isomers of sulfide **10** and its monomer.

Introduction

The chemistry of hypervalent organoantimony compounds[1–4] containing one pendant arm (*C*,*N*)-ligand such as 2-[Me_2NCH-(R)]C_6H_4 [R = H,[5] Me[5h,6]] or 2-[$O(CH_2CH_2)_2NCH_2]C_6H_4$,[7] "pincer"-type ligands like symmetric 2,6-$(Me_2NCH_2)_2C_6H_3$ [(*N*,*C*,*N*)-ligand],[8] 2,6-$(ROCH_2)_2C_6H_3$ [(*O*,*C*,*O*)-ligand],[8e,9] asymmetric 2-(Me_2NCH_2)-6-$(ROCH_2)C_6H_3$ [(*N*,*C*,*O*)-ligand],[10] or $E(CH_2C_6H_4)_2$ (E = RN, O, S) groups,[3,4] which all can be considered as dianionic (*C*,*E*,*C*)-ligands, aroused in recent years considerable interest with regard to both fundamental research and applications. Such ligands can protect the metal centre by increased coordination through intramolecular E → Sb (E = N, O, S) interactions observed both in the solid state and in solution, thus providing thermodynamical stabilization and allowing isolation of unusual species, *e.g.* heterocyclic organoantimony sulfides, $(RSbS)_2$. Hypervalent [2,6-$(Me_2NCH_2)_2C_6H_3SbE]_2$ (E = O, S) can be used to trap CO_2 or CS_2; these compounds were found to react reversibly with CO_2 or CS_2 in solution.[8f,j] Also their use as reagents or as catalysts in organic synthesis (*e.g.* cross-coupling reactions[11,12]) was reported.

In contrast to hypervalent organoantimony compounds containing ligands with an sp^3-nitrogen atom in the pendant arm, related species based on intramolecular N(sp^2) → Sb interactions were much less investigated. For example [2-{RN=CH}$C_6H_4]_3Sb$ [R = (*R*)-$MeC_6H_4CH(Me)$, (*R*)-$HOCH_2CH$-(Et)][13] was obtained by condensation of RNH_2 with [2-(O=CH)-$C_6H_4]_3Sb$.[14] Hypercoordination in tetraarylstibonium salts was related to the presence of an internal N → Sb interaction in

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†Electronic supplementary information (ESI) available: X-ray crystallographic data in CIF format for **4**, **5**, **6**·$CHCl_3$, **7**, **9**·CH_2Cl_2, **10** and **11**·0.25CH_3OH; figures representing the optical isomers as well as the supramolecular architectures in the crystals of these compounds; NMR spectra; representations of calculated *vs.* determined structures of the *all-trans* dimer association of **7** and of the *all-trans* isomer of **10**; selected calculated and experimental bond lengths and angles for the *all-trans* dimer of **7** and the *all-trans* isomer of **10**; atomic coordinates for the optimized models. CCDC 821266 (**4**), 821267 (**5**), 821268 (**6**·$CHCl_3$), 821269 (**7**), 821270 (**9**·CH_2Cl_2), 821271 (**10**) and 821272 (**11**·0.25CH_3OH). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt32494f

$[RSbR'_3][CuI_2]$ [R = 2-(4-$MeOC_6H_4N{=}CH)C_6H_4$, 2-(3,5-X_2-4-$HOC_6H_2N{=}CH)C_6H_4$ (X = Cl, Br, Ph)][15a] and [2-(4-$MeOC_6H_4N{=}CH)C_6H_4SbPh_3]_4[Cu_{14}I_{18}]$.[15b] A remarkable achievement was the isolation of an RSb(I) monomer using the pincer (*N*,*C*,*N*)-ligand R = 2,6-[2′,6′-$Me_2C_6H_3N{=}C(Me)]_2C_6H_3$.[16] Recently, while this work was under progress,[17] organoantimony compounds such as R_nSbCl_{3-n} (n = 1,2), R_4Sb_2 and *cyclo*-$(RSb)_4$ [R = 2-(2′,6′-$iPr_2C_6H_3N{=}CH)C_6H_4$] were reported.[18]

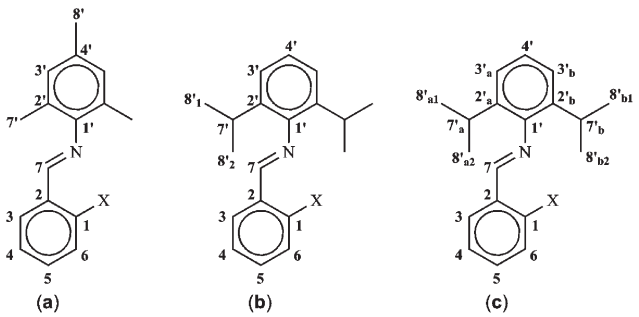
As part of our interest in organoantimony(III) compounds with pendant arms we report herein the synthesis, spectroscopic characterization and crystal structures of species (bromides and chalcogenides) containing (imino)aryl ligands of the type 2-$(RN{=}CH)C_6H_4$ (R = 2′,4′,6′-$Me_3C_6H_2$, 2′,6′-$^iPr_2C_6H_3$). The chemistry of these compounds with rigid and sterically demanding organic groups is compared with that of related organoantimony(III) species containing the 2-$(Me_2NCH_2)C_6H_4$ ligand.[5g,i,j]

Results and discussion

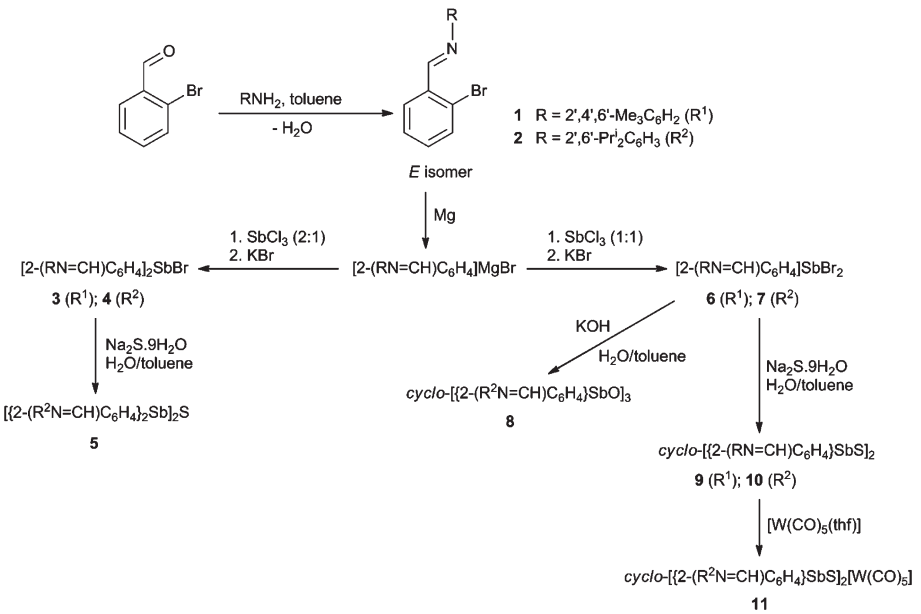
Synthesis and characterization of organoantimony(III) bromides

The organic bromides 2-$(RN{=}CH)C_6H_4Br$ [R = 2′,4′,6′-$Me_3C_6H_2$ (R^1) (**1**), 2′,6′-$^iPr_2C_6H_3$ (R^2) (**2**)] were obtained as *E* isomers by condensation of 2-bromobenzaldehyde with the corresponding aromatic amine according to a slightly modified literature method reported for **2** (Scheme 1).[19] Both compounds were isolated as yellow solids after recrystallization from hexane (85% for **1**, 76% for **2**). Treatment of the Grignard reagents RMgBr with $SbCl_3$ in a 2 : 1 and 1 : 1 molar ratio gave mixtures of chloride/bromide R_2SbX and $RSbX_2$ derivatives, respectively, due to partial halogen exchange reactions. Following treatment of the crude organoantimony halides in CH_2Cl_2 with an aqueous solution of KBr the pure bromides R_2SbBr and $RSbBr_2$ were isolated as yellow solids (yields in the range 37–53%). Both the organic bromides **1** and **2** and the organoantimony(III) bromides $[2\text{-}(R^1N{=}CH)C_6H_4]_2SbBr$ (**3**) and $[2\text{-}(R^2N{=}CH)C_6H_4]_2SbBr$ (**4**) as well as dibromides $[2\text{-}(R^1N{=}CH)\text{-}C_6H_4]SbBr_2$ (**6**) and $[2\text{-}(R^2N{=}CH)C_6H_4]SbBr_2$ (**7**) are well soluble in chlorinated solvents (CH_2Cl_2, $CHCl_3$). NMR data of **1–4**, **6** and **7** as well as elemental analytical data are consistent with the anticipated formulas. The EI mass spectra of the organic bromides **1** and **2** show the corresponding molecular ions. For the $[2\text{-}(RN{=}CH)C_6H_4]_nSbBr_{3-n}$ (n = 2, 1) species (compounds **2**, **4**, **6**, **7**) the base peaks in the ESI+ mass spectra are assigned to $[R_2Sb^+]$ and $[RSbBr^+]$ fragments for the monobromides $[2\text{-}(RN{=}CH)C_6H_4]_2SbBr$ and dibromides $[2\text{-}(RN{=}CH)C_6H_4]SbBr_2$, respectively.

The NMR spectra of **1–4**, **6** and **7** were recorded in $CDCl_3$ at room temperature. The assignment of resonances in the ^1H and ^{13}C NMR spectra was based on 2D NMR (HSQC, HMBC and COSY) correlation spectra, according to the numbering schemes shown in Scheme 2. The spectra of the dibromides **6**



Scheme 2 Numbering scheme for NMR assignments.



Scheme 1 Preparation of compounds **1–11**.

and **7** show one set of resonances for the substituents in *ortho* positions as well as for the *meta* positions of the aromatic R group attached to nitrogen, consistent with the presence of only one species in solution for which free rotation around the C–N(=C) single bond is not restricted. The presence of two doublets for the methyl protons of the ^{i}Pr groups in **7** indicates their diastereotopic nature. No essential changes were observed when the ^{1}H NMR spectrum of **7** was recorded in $CDCl_3$ at −60 °C.

Significant differences should be noted in the solution behaviour of the bromides **3** and **4**. For **3** both ^{1}H and ^{13}C NMR spectra exhibit only one set of aromatic resonances and one resonance for the *imine* protons (δ 8.29 ppm). This is consistent with equivalence of the organic groups attached to antimony at the NMR time scale, which suggests a fast fluxional behaviour, *i.e.* coordination–decoordination of the nitrogen atoms. Moreover, the presence of two sharp resonances at δ 1.65 and 2.20 ppm (2 : 1 integral ratio) assigned to methyl protons indicates that there is no restriction of free rotation of the mesityl groups around the C–N(=C) single bonds. It should be noted that in the case of the related [2-(Me_2NCH_2)-C_6H_4]$_2$SbCl the dynamic process resulting in equivalent organic ligands is frozen only at −60 °C, while at room temperature the ^{1}H NMR spectrum shows one set of broad resonances.[5g] By contrast, the room temperature NMR spectra for **4** show two sets of resonances indicating that the organic groups in this molecule are not equivalent as was also observed in the solid state (see subsequent discussion) due to the coordination of nitrogen atoms *trans* to bromine or to an aromatic carbon attached to the metal atom, respectively. A similar pattern was also observed at room temperature for the analogous chloride, [2-(2′,6′-$^{i}Pr_2C_6H_3N$=CH)C_6H_4]$_2$SbCl.[18] This is clearly evidenced by the presence of two sharp singlet resonances in the aromatic region, assigned to the *imine* protons of the non-equivalent organic substituents (δ 8.36 and 8.43 ppm, respectively). Moreover, the ^{1}H (see Fig. 1) and ^{13}C NMR (see ESI, Fig. S3 and S4†) spectra indicate that for one ligand unit (designated by **B**) free rotation around the C–N(=C) single bond is not restricted (*e.g.* one singlet resonance at δ 27.77 ppm for C-7′ atoms; Scheme 2b) and for the other substituent (designated by **A**) the free rotation of the bulky 2,6-$^{i}Pr_2C_6H_3$ group is blocked. This results in non-equivalence of the two halves of this aromatic moiety (Scheme 2c) as indicated, for example, by the presence of two singlet resonances at δ 28.00 and 28.48 ppm for C-7′$_a$ and C-7′$_b$, respectively. The different behaviour of **3** and **4** in $CDCl_3$ solution at room temperature might be related to the bulkiness of the organic group attached to nitrogen.

The IR stretching vibration of the carbon–nitrogen double bond appears in the 1650–1550 cm^{-1} region as is typical for compounds containing Schiff-base ligands. In the IR spectra of the title organoantimony(III) bromides the $\nu_{C=N}$ stretching vibration was observed at 1624 (for **3**), 1634 (for **4**), 1617 (for **6**) and 1621 cm^{-1} (for **7**), respectively. This pattern might be consistent with the presence of intramolecular N → Sb coordination and a delocalization of the π electrons of the –C=N– bond over the resulting C_3NSb ring.

Single crystals suitable for X-ray diffraction studies were obtained by slow diffusion of *n*-hexane into CH_2Cl_2 (**4** and **7**) or $CHCl_3$ (**6**·$CHCl_3$) solutions. The solid state molecular structures of these bromides are depicted in Fig. 2–4. Selected interatomic distances and angles are summarized in Tables 1 and 2.

As expected, a common feature for the solid state structure of the title compounds is that the *imine* nitrogen is coordinated intramolecularly to the antimony atom. In related compounds with pendant arms which contain an sp^3-carbon atom between the aromatic ring and the donor atom [*e.g.* 2-[$Me_2NCH(R)$]C_6H_4, 2-[$O(CH_2CH_2)_2NCH_2$]C_6H_4, 2,6-$(ROCH_2)_2$-C_6H_3] a five-membered C_3SbE chelate ring with internal E → Sb (E = N, O) interaction results. This ring is folded along the Sb···$C_{methylene}$ axis and this induces planar chirality.[4,5m] In contrast, the presence of the –C=N– bond in the pendant arm results in a planar C_3SbN unit and thus the title compounds do not anymore exhibit planar chirality. However, the intramolecular N(sp^2) → Sb interaction results in "*chelate induced-Sb-chiral*" compounds.[4,5m] The organic ligands in **4** become non-equivalent since the nitrogen atoms are coordinated to

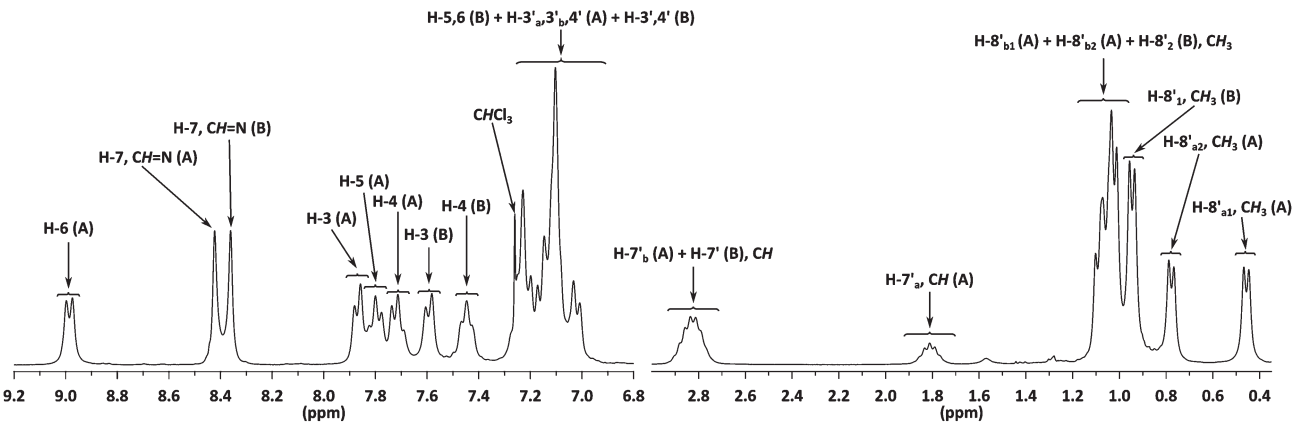


Fig. 1 ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of compound **4**, at room temperature.

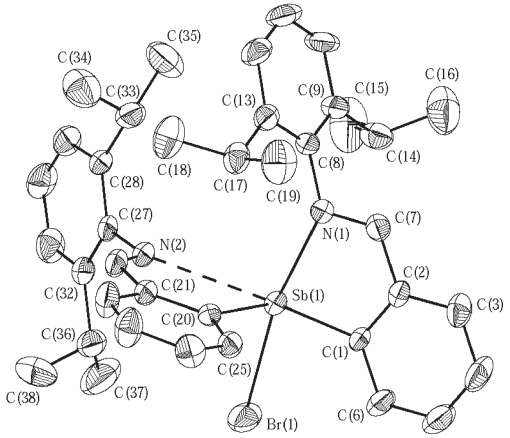


Fig. 2 ORTEP representation at 30% probability and atom numbering scheme for the (C_{Sb})-**4** isomer.

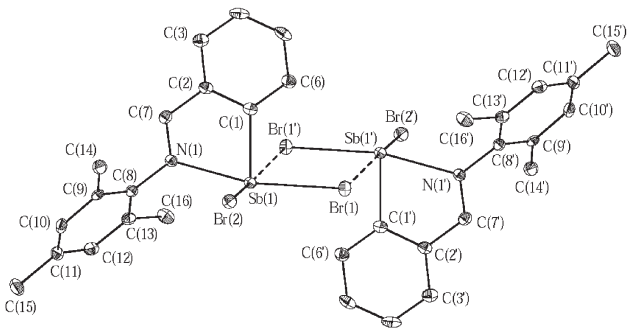


Fig. 3 ORTEP representation at 40% probability and atom numbering scheme for the dimer association between (C_{Sb})- and (A_{Sb})-**6** isomers in the crystal of **6**·$CHCl_3$ (the solvent molecule is not shown) [symmetry equivalent atoms (2 – *x*, –*y*, 1 – *z*) are given by "prime"].

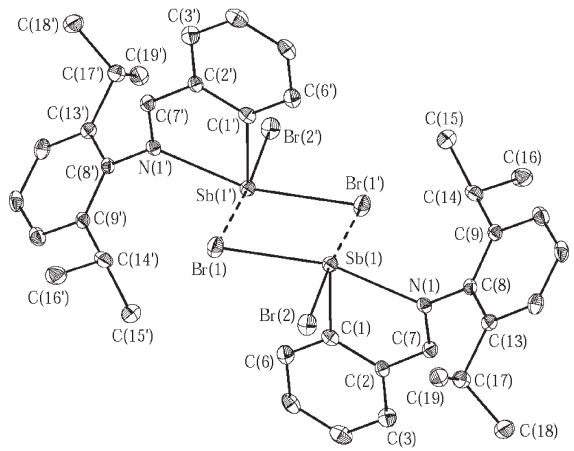


Fig. 4 ORTEP representation at 40% probability and atom numbering scheme for the dimer association between (C_{Sb})- and (A_{Sb})-**7** isomers in the crystal of **7** [symmetry equivalent atoms (1 – *x*, 1 – *y*, 1 – *z*) are given by "prime"].

antimony *trans* to different atoms. Similarly, in **6** and **7** the two halogen atoms per molecule are not equivalent following the coordination of the nitrogen in the *trans* position to one of them. In both diorgano- and monoorganoantimony(III) derivatives the chirality thus induced at the metal atom can be described in terms of C_{Sb} and A_{Sb} isomers[20] for the square pyramidal $(C,N)_2SbBr$ (hypervalent 12-Sb-5 species) and *pseudo*-trigonal bipyramidal ("*see-saw*") $(C,N)SbBr_2$ cores (hypervalent 10-Sb-4 species), respectively.[1,21] Indeed, the crystals of the title bromides contain a 1 : 1 mixture of these isomers.

Table 1 Selected bond distances (Å) and angles (°) for compounds **4** and **5**

	4	**5**
Sb(1)–C(1)	2.165(5)	2.167(2)
Sb(1)–C(20)	2.153(5)	2.163(2)
Sb(1)–E(1)[a]	2.6371(11)	2.4727(6)
Sb(1)–N(1)	2.498(4)	2.616(2)
Sb(1)–N(2)	2.996(4)	
N(1)–C(7)	1.277(6)	1.277(3)
N(1)–C(8)	1.444(6)	1.432(3)
N(2)–C(26)	1.252(7)	1.264(3)
N(2)–C(27)	1.423(6)	1.432(3)
C(1)–Sb(1)–C(20)	95.84(19)	101.00(8)
E(1)–Sb(1)–C(1)[a]	93.15(14)	97.01(5)
E(1)–Sb(1)–C(20)[a]	90.88(13)	91.77(5)
N(1)–Sb(1)–C(1)	72.92(17)	71.19(7)
N(1)–Sb(1)–C(20)	86.43(16)	83.66(6)
N(1)–Sb(1)–E(1)[a]	165.43(10)	166.14(3)
N(1)–Sb(1)–N(2)	102.00(13)	
N(2)–Sb(1)–C(1)	163.75(16)	
N(2)–Sb(1)–C(20)	68.20(16)	
N(2)–Sb(1)–E(1)[a]	90.24(9)	
Sb(1)–E(1)–Sb(1a)[ab]		88.57(3)
C(7)–N(1)–C(8)	117.6(4)	119.81(17)
Sb(1)–N(1)–C(7)	108.2(3)	106.2(1)
Sb(1)–N(1)–C(8)	130.1(3)	126.6(1)
C(26)–N(2)–C(27)	119.9(5)	118.68(18)
Sb(1)–N(2)–C(26)	99.4(4)	
Sb(1)–N(2)–C(27)	140.6(3)	

[a] E(1) = Br(1) for **4**, and S(1) for **5**. [b] Symmetry equivalent atoms (–*x*, *y*, 0.5 – *z*) are given by "a".

As expected, in the bromide **4** the length of the internal N → Sb interactions is different, *i.e.* that one established *trans* to the bromine atom [Sb(1)–N(1) 2.498(4) Å; N(1)–Sb(1)–Br(1) 165.43(10)°] being shorter than that one established *trans* to the carbon atom [Sb(1)–N(2) 2.996(4) Å; N(2)–Sb(1)–C(1) 163.75(16)°; *cf.* sums of the corresponding covalent, Σr_{cov}(Sb,N) 2.11 Å, and van der Waals radii, Σr_{vdW}(Sb,N) 3.74 Å].[22] The lengths of these N → Sb bonds are similar to those reported for the analogous chloride [Sb(1)–N(1) 2.416(2) Å; Sb(1)–N(2) 2.952(3) Å]. When compared to the N → Sb interactions in the related $[2\text{-}(Me_2NCH_2)C_6H_4]_2SbBr$ [Sb(1)–N(1) 2.423(3) Å; Sb(1)–N(2) 3.276(3) Å][5g] the significant decrease of the interatomic distance corresponding to the N → Sb interaction *trans* to the carbon atom is remarkable. This behaviour is a consequence of the better donor properties of a N(sp^2) atom *versus* a N(sp^3) atom.

The antimony–nitrogen distance in the dibromides **6** [Sb(1)–N(1) 2.346(3) Å] and **7** [Sb(1)–N(1) 2.395(3) Å] is shorter

Table 2 Selected bond distances (Å) and angles (°) for compounds **6**·$CHCl_3$, **7**, **9**·CH_2Cl_2 and **10**

	6·$CHCl_3$	**7**		**9**·CH_2Cl_2	**10**
Sb(1)–C(1)	2.149(3)	2.162(3)	Sb(1)–C(1)	2.161(3)	2.162(4)
Sb(1)–Br(1)	2.8034(5)	2.7174(7)	Sb(1)–S(1)	2.5326(9)	2.5269(9)
Sb(1)–Br(2)	2.5749(5)	2.5426(7)	Sb(1)–S(1′)	2.4016(9)[c]	2.4167(10)[d]
Sb(1)–N(1)	2.346(3)	2.395(3)	Sb(1)–N(1)	2.553(2)	2.558(2)
Sb(1)–Br(1′)	3.2050(5)[a]	3.3362(5)[b]			
N(1)–C(7)	1.285(5)	1.283(3)	N(1)–C(7)	1.264(4)	1.261(4)
N(1)–C(8)	1.432(5)	1.432(4)	N(1)–C(8)	1.436(4)	1.436(4)
C(1)–Sb(1)–Br(1)	90.70(10)	91.86(8)	C(1)–Sb(1)–S(1)	95.09(8)	94.37(8)
C(1)–Sb(1)–Br(2)	92.42(11)	93.16(8)	C(1)–Sb(1)–S(1′)	100.15(8)	99.54(8)
Br(1)–Sb(1)–Br(2)	87.14(1)	89.61(1)	S(1)–Sb(1)–S(1′)	88.69(3)	89.08(3)
N(1)–Sb(1)–C(1)	75.45(12)	74.84(10)	N(1)–Sb(1)–C(1)	72.25(10)	72.39(11)
N(1)–Sb(1)–Br(1)	163.60(7)	164.82(5)	N(1)–Sb(1)–S(1)	161.88(6)	161.56(6)
N(1)–Sb(1)–Br(2)	84.76(7)	83.97(6)	N(1)–Sb(1)–S(1′)	81.12(6)	80.82(6)
Br(1′)–Sb(1)–C(1)	80.55(11)	77.61(7)			
Br(1′)–Sb(1)–Br(1)	87.53(1)	91.76(1)			
Br(1′)–Sb(1)–Br(2)	171.12(1)	170.70(1)			
Br(1′)–Sb(1)–N(1)	98.59(7)	92.44(6)			
Sb(1)–Br(1′)–Sb(1′)	92.47(1)	88.24(1)	Sb(1)–S(1′)–Sb(1′)	91.31(3)	90.93(3)
C(7)–N(1)–C(8)	120.9(3)	120.8(3)	C(7)–N(1)–C(8)	120.4(3)	119.3(3)
Sb(1)–N(1)–C(7)	111.7(2)	111.2(2)	Sb(1)–N(1)–C(7)	109.00(19)	108.9(2)
Sb(1)–N(1)–C(8)	127.0(2)	127.99(17)	Sb(1)–N(1)–C(8)	130.60(18)	131.2(2)

[a] Symmetry equivalent atoms $(2 - x, -y, 1 - z)$ are given by "prime". [b] Symmetry equivalent atoms $(1 - x, 1 - y, 1 - z)$ are given by "prime". [c] Symmetry equivalent atoms $(1 - x, -y, -z)$ are given by "prime". [d] Symmetry equivalent atoms $(-x, -y, 2 - z)$ are given by "prime".

than in **4**. This is as a result of a combined effect produced by the hybridization nature of the donor atom [$N(sp^2)$] and the increased Lewis acidity of the metal atom with an increasing number of halogen atoms attached to it [to be compared with [2-$(Me_2NCH_2)C_6H_4$]$SbBr_2$:[5g] Sb(1)–N(1) 2.409(3) Å].

While no intermolecular interactions between heavy atoms were observed in the bromide **4**, the molecules of the dibromides are associated into centrosymmetric dimer units built from C_{Sb} and A_{Sb} isomers through asymmetric bromine bridges involving the halogen *trans* to nitrogen (Fig. 3 and 4). As expected, for the molecular unit of the dibromides **6** and **7** the terminal Sb–Br bond is much shorter than that involved in the bromine Sb–Br···Sb bridge, while the Sb–Br bond in **4** is of intermediate length between the values observed for the dibromides (see Tables 1 and 2). The overall coordination geometry around the metal becomes square pyramidal [(*C*,*N*)$SbBr_3$ core] in **6** and **7** if the intermolecular antimony–bromine interaction [Sb(1)–Br(1a) 3.2050(5) Å for **6** and 3.3362(5) Å for **7**, respectively] is taken into account (hypervalent 12-Sb-5 species).[1,21] The *trans* orientation of the Sb–C, terminal Sb–Br and Sb–N bonds of the two molecules in the dimer unit with respect to the central planar Sb_2Br_2 ring should be noted (see also the Theoretical calculations section). A similar asymmetric dimer association was described for the related [2-$(Me_2NCH_2)C_6H_4$]-$SbBr_2$.[5g] In contrast, the crystal of the chloride analogue, [2-(2′-,6′-$^{i}Pr_2C_6H_3N{=}CH)C_6H_4$]$SbCl_2$, was reported to contain only discrete molecules, without intermolecular interactions between heavy atoms.[18]

Intramolecular Br···H contacts are established in the molecule of **4** [Br(1)···$H(6)_{aryl}$ 2.81 Å; Br(1)···$H(36)_{methine}$ 2.95 Å]. In addition, a closer look revealed both intra- and intermolecular C–H···π ($Ph_{centroid}$) distances consistent with π interactions between hydrogen atoms of one ^{i}Pr group and the aromatic rings attached to the metal (*i.e.* H···$Ph_{centroid}$ contacts shorter than 3.1 Å, with an angle γ between the normal to the aromatic ring and the line defined by the H atom and $Ph_{centroid}$ smaller than 30°):[23] C(17)–$H(17)_{methine}$···$Ph_{centroid}${C(20)–C(25)} 2.84 Å, γ = 19.4°, and C(19)–$H(19C)_{methyl}$···$Ph_{centroid}${C(1a)–C(6a)} 2.76 Å, γ = 9.7°. The latter one results in the formation of polymeric chains of (C_{Sb})-**4** and (A_{Sb})-**4** isomers, respectively, without further contacts between parallel chains (for details, see ESI†).

As in the case of the monobromide **4**, an intramolecular Br···H contact is established in the molecules of **6** or **7** [Br(1)···$H(6)_{aryl}$ 2.80 Å]. In addition, further Br···H contacts are established between the two halves of the centrosymmetric dimer units [Br(1)···$H(16A')_{methyl}$ 3.10 Å in **6**; Br(1)···$H(14')_{methine}$ 2.93 Å in **7**]. In the crystal of **6**·$CHCl_3$ the dimer units are connected through weak C–H···π ($Ph_{centroid}$) interactions [C(15)–$H(15C)_{methyl}$···$Ph_{centroid}${C(8′a)–C(13′a)} 2.99 Å, γ = 24.1°] into chain polymers of alternating (C_{Sb})- and (A_{Sb})-**6** isomers. Each chain is further connected to four other parallel chains through weak Br···H contacts [Br(2)···$H(7)_{imine}$ 3.05 Å] which involve the terminal bromine atoms of the dimer units. By contrast, the crystal of **7** contains layers in which a dimer unit is connected to four other dimers through C–H···π ($Ph_{centroid}$) [C(3)–$H(3)_{aryl}$···$Ph_{centroid}${C(8a)–C(13a)} 2.92 Å, γ = 13.4°] and

Br···H [Br(2a) ···H(16B)$_{methyl}$ 2.96 Å] contacts (for details, see ESI†).

Synthesis and characterization of organoantimony(III) chalcogenides

The synthesis of organoantimony(III) chalcogenides was based on previously developed mixed-solvent procedures,[5i,j] *i.e.* reaction of **7** with KOH or the bromides **4**, **6** or **7** with $Na_2S{\cdot}9H_2O$, in water–toluene mixtures (Scheme 1). The compounds were isolated as colourless (oxide **8**) or yellow to orange solids (sulfides **5**, **9**, **10**). Treatment of the heterocyclic sulfide **10** with $[W(CO)_5(thf)]$ in a 1 : 1 molar ratio gave the metal carbonyl complex *cyclo*-[{2-(2′,6′-$^{i}Pr_2C_6H_3N{=}CH)C_6H_4$}SbS]$_2$[$W(CO)_5$] (**11**) as an orange-brown solid. The IR bands in the range 1618–1628 cm^{-1} are assigned to the $\nu_{C=N}$ stretching vibration, which is consistent with the presence of the imine ligand in the title chalcogenides. The IR spectrum of **11** shows the typical pattern for complexes containing a $W(CO)_5$ fragment. The molecular ion [M$^+$] was observed in the EI MS of *cyclo*-[{2-(2′,4′,6′-$Me_3C_6H_2N{=}CH)C_6H_4$}SbS]$_2$ (**9**). The ESI+ mass spectra of *cyclo*-[{2-($R^2N{=}CH)C_6H_4$}SbO]$_3$ (**8**) and *cyclo*-[{2-($R^2N{=}CH$)-C_6H_4}SbS]$_2$ (**10**) (R^2 = 2′,6′-$^{i}Pr_2C_6H_3$) show the corresponding molecular [M$^+$ + H] ions, while for [{2-(2′,6′-$^{i}Pr_2C_6H_3N{=}CH$)-C_6H_4}$_2$Sb]$_2$S (**5**) the ion [M$^+$ − H] was observed. For the complex **11** an [M$^+$ – CO] ion was assigned to the base peak.

The ^{1}H and ^{13}C NMR spectra, recorded in $CDCl_3$ at room temperature, provide evidence for some particular behaviour in solution for these chalcogenides. The assignment of resonances was based on 2D NMR (HSQC, HMBC and COSY) correlation spectra, according to the numbering schemes shown in Scheme 2. The ^{1}H NMR spectrum of the sulfide **5** shows only one set of broad resonances, including that for the *imine* protons (δ 8.34 ppm). This behaviour suggests a quite fast dynamic process on the NMR time scale to give four equivalent organic groups attached to antimony atoms in this dinuclear species. A similar solution behaviour was previously described for the related compound [{2-(Me_2NCH_2)C_6H_4}$_2$Sb]$_2$S.[5j]

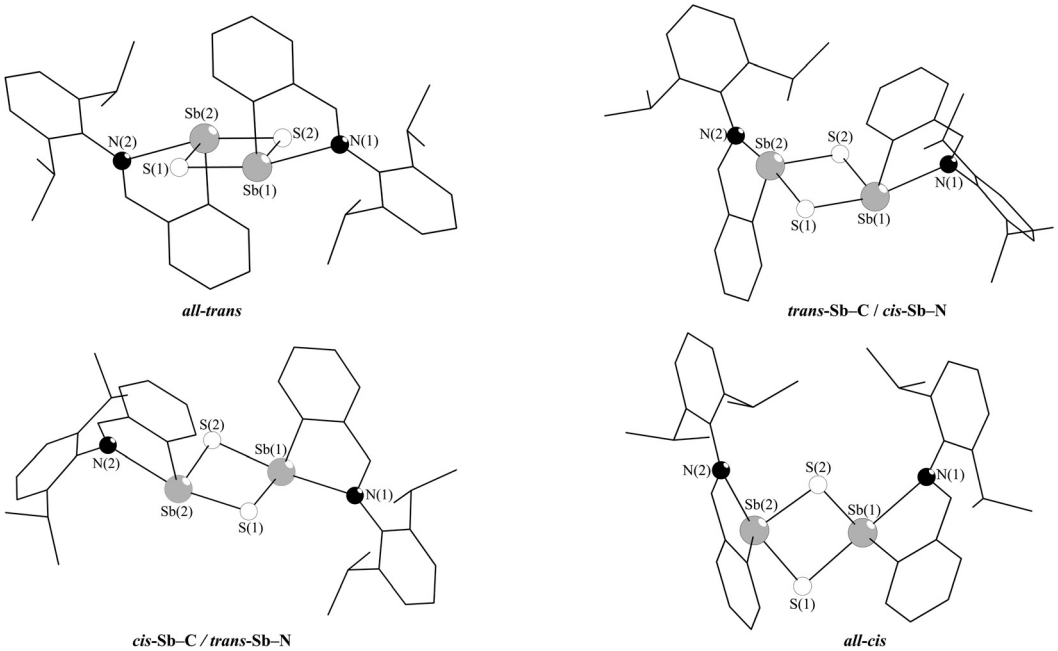
The ^{1}H and ^{13}C NMR spectra of the oxide **8** show two sets of resonances. While the ^{1}H resonances in the aliphatic region are not well separated, those in the aromatic region indicate a 2 : 1 integral ratio for equivalent protons, *e.g.* δ 8.35 (2 H) and 8.36 (1 H) ppm for *imine* protons. This suggests the presence of a trimer species in solution, with *cis* and *trans* organic substituents with respect to an Sb_3O_3 heterocycle. A trimer species is consistent with the molecular [M$^+$ + H] ion observed in the ESI+ mass spectrum of **8**. It should be noted that a similar behaviour in solution was reported for the organic groups in *cyclo*-[{2-(Me_2NCH_2)C_6H_4}SbO]$_3$, for which the trimeric nature was also established by single-crystal X-ray structure analysis.[5i]

For both heterocyclic sulfides **9** and **10** the NMR spectra (in $CDCl_3$, at r.t.) contain two sets of resonance signals both in the alkyl and aryl region. The corresponding integral ratio based on the resonances for the H-6 (for **9**) and H-4 (for **10**) protons (see Scheme 2) is 1.4 : 1 and 1.8 : 1, respectively. No significant changes were observed when the ^{1}H NMR spectrum of **9** was recorded in $CDCl_3$ at −60 °C. Taking into account the results obtained by single-crystal X-ray diffraction (see subsequent discussion) and the behaviour in solution which suggests the absence of ring–ring equilibria, it might be concluded that the oligomerization degree observed in the solid state, *i.e.* dimer species, is preserved in chloroform solution. A similar situation was reported previously for the related *cyclo*-[{2-(Me_2NCH_2)C_6H_4}SbS]$_2$.[5i] Several isomers can be then considered for sulfides of the type *cyclo*-[{2-($RN{=}CH)C_6H_4$}SbS]$_2$ with the relative orientation of the Sb–C and Sb–N bonds, *i.e.* *all-trans*, *trans*-Sb–C/*cis*-Sb–N, *cis*-Sb–C/*trans*-Sb–N, and *all-cis*, respectively, with respect to an Sb_2S_2 ring (Scheme 3). Although the two sets of resonances could not be assigned to a particular isomer, one can assume that the *all-trans* and *all-cis* isomers (see subsequent discussion on compound **11**) are most likely to be present in the chloroform solution of the *cyclo*-[{2-($RN{=}CH)C_6H_4$}SbS]$_2$ derivatives.

The ^{1}H NMR spectrum of the metal carbonyl complex **11** shows one set of broad singlets or poor resolved multiplets, consistent with equivalent organic ligands attached to the antimony atoms and a dynamic process at room temperature. The number of ^{13}C resonances assigned to aliphatic carbons and the broad signal for the C-3′ aromatic carbons suggest that the free rotation around the C–N(=C) single bond is restricted. The presence of the $W(CO)_5$ moiety is indicated by a singlet resonance surrounded by ^{183}W satellites, assigned to the equatorial CO groups.

Single crystals of **5**, **9**·CH_2Cl_2 and **10** were obtained by slow diffusion of *n*-hexane into CH_2Cl_2 solutions. Crystals of **11**·0.25CH_3OH were similarly grown using a *n*-hexane–CH_2Cl_2 system (3 : 1) (methanol was used as the stabilizing agent for methylene chloride). The solid state molecular structures of these sulfides are depicted in Fig. 5–8. Selected interatomic distances and angles are listed in Tables 1 (for **5**), 2 (for **9**·CH_2Cl_2 and **10**) and 3 (**11**·0.25CH_3OH).

In contrast to the bromide **4** used as a starting material to prepare **5**, the sulfide exhibits only one internal N → Sb interaction per metal atom, placed *trans* to the Sb–S bond [N(1)–Sb(1)–S(1) 166.14(3)°] (Fig. 5). The pendant arm of the second organic ligand attached to the antimony atom is twisted to bring the nitrogen atom N(2) as far as possible from the metal. The antimony–nitrogen distance is intermediate [N(1)–Sb(1) 2.616(2) Å] between those observed in the molecule of **4** (Table 1) and considerably shorter than the shortest N → Sb interaction [2.855(3) Å] in [{2-(Me_2NCH_2)C_6H_4}$_2$Sb]$_2$S.[5j] The result is a *pseudo*-trigonal bipyramidal coordination environment for antimony in **5** [(*C*,*N*)CSbS core; hypervalent 10-Sb-4 species].[1,21] This behaviour is clearly due to the steric stress produced by the Sb(1)–S(1)–Sb(1′) angle [88.57(3)°] which brings the bulky [{2-(2′,6′-$^{i}Pr_2C_6H_3N{=}CH)C_6H_4$}$_2$Sb] moieties in close proximity. It should be noted that the antimony–sulfur bond distances are similar in the molecules of **5** [Sb(1)–S(1) 2.4727(6) Å] and the related [{2-(Me_2NCH_2)C_6H_4}$_2$Sb]$_2$S [Sb(1)–S(1) 2.4621(10) Å], but the Sb(1)–S(1)–Sb(1′) angle in the latter species is much more opened [100.78(5)°]. For [{2-(Me_2NCH_2)C_6H_4}$_2$Sb]$_2$S this allows a square pyramidal (*C*,*N*)$_2$SbS core for both metal atoms to which, in addition, less bulky organic ligands are attached.[5j]



Scheme 3 Potential geometric isomers for the heterocyclic sulfide **10** with respect to a planar Sb_2S_2 ring.

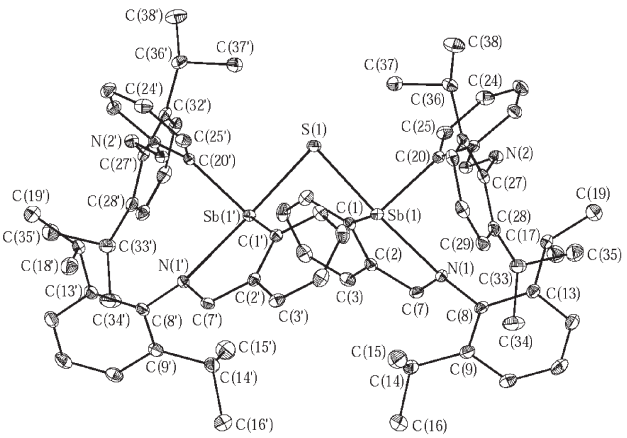


Fig. 5 ORTEP representation at 30% probability and atom numbering scheme for the (C_{Sb},$C_{Sb'}$)-**5** isomer [symmetry equivalent atoms (–*x*, *y*, 0.5 – *z*) are given by "prime"].

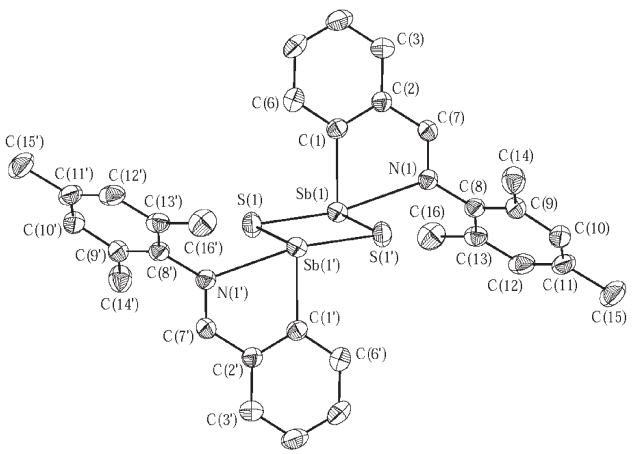


Fig. 6 ORTEP representation at 40% probability and atom numbering scheme for the (A_{Sb},$C_{Sb'}$)-**9** isomer [symmetry equivalent atoms (1 – *x*, –*y*, –*z*) are given by "prime"].

For both heterocyclic sulfides the crystals contain only discrete dinuclear units of the *all-trans* (A_{Sb},$C_{Sb'}$)-**9** (Fig. 6) and (C_{Sb},$A_{Sb'}$)-**10** (Fig. 7) isomers with a crystallographically imposed inversion symmetry. The overall molecular structures are very similar to that described for the related *cyclo*-[{2-(Me_2NCH_2)C_6H_4}SbS]$_2$.[5i] The molecules contain a central, planar four-membered Sb_2S_2 ring, with endocyclic angles at antimony and sulfur atoms close to 90° (Table 2). In the molecular unit the (*N*,*C*)-ligands are placed on opposite sides of the Sb_2S_2 ring. The asymmetry of the ring is reflected in alternating short [Sb(1)–S(1′) 2.4016(9) and 2.4167(10) Å for **9** and **10**, respectively] and long [Sb(1)–S(1) 2.5326(9) and 2.5269(9) Å for **9** and **10**, respectively] antimony–sulfur bonds. The coordination of a nitrogen atom *trans* to each sulfur atom accounts for the elongation of the corresponding antimony–sulfur bonds. As expected for a N(sp^2) donor atom, the Sb(1)–N(1) bond distance [2.553(2) and 2.558(2) Å for **9** and **10**, respectively] is shorter than that observed for a N(sp^3) donor atom in *cyclo*-[{2-(Me_2NCH_2)C_6H_4}SbS]$_2$ [Sb(1)–N(1) 2.634(4) Å].[5i]

While the reaction of *cyclo*-[$(Me_3Si)_2CHSbS]_n$ (n = 2, 3) and [$W(CO)_5$(thf)] gave the complex *cyclo*-[$(Me_3Si)_2CHSbS]_2$-[$W(CO)_5]_2$ with metal carbonyl units coordinated to the Sb atoms,[24] the complex **11** was found to contain a $W(CO)_5$ fragment coordinated to a sulfur atom as in the related *cyclo*-[{2-(Me_2NCH_2)C_6H_4}SbS]$_2$[$W(CO)_5$].[5i] However there is an important difference in the molecular structures of these 1 : 1 adducts. In *cyclo*-[{2-(Me_2NCH_2)C_6H_4}SbS]$_2$[$W(CO)_5$] the metal

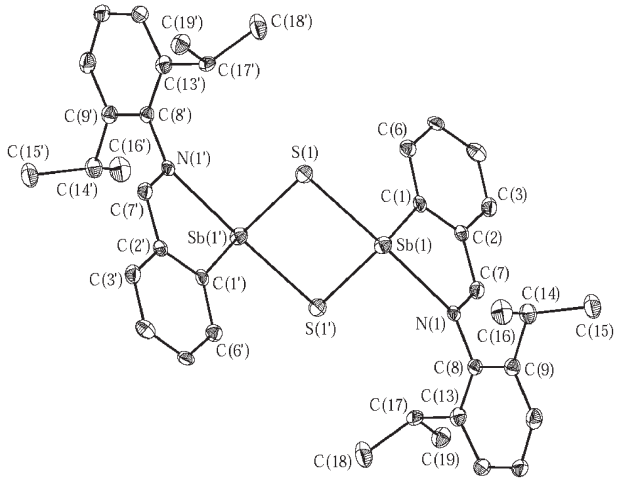


Fig. 7 ORTEP representation at 40% probability and atom numbering scheme for the (C_{Sb},$A_{Sb'}$)-**10** isomer [symmetry equivalent atoms (–*x*, –*y*, 2 – *z*) are given by "prime"].

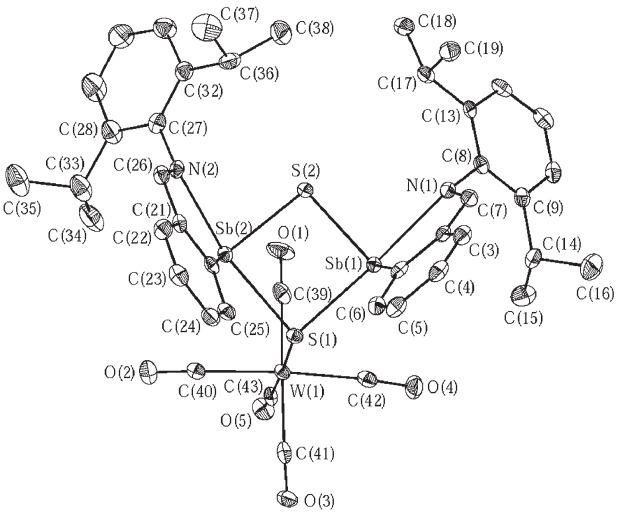


Fig. 8 ORTEP representation at 40% probability and atom numbering scheme for the (C_{Sb1},A_{Sb2})-**11** isomer.

carbonyl unit is coordinated to the *cis*-Sb–C/*trans*-Sb–N isomer of the heterocyclic sulfide.[5i] In contrast, in the molecule of the complex **11** a $W(CO)_5$ fragment is coordinated to the *all-cis* isomer of the sulfide **10** (Fig. 8), occupying a *trans* position relative to the organic ligands with respect to the Sb_2S_2 ring. Both nitrogen atoms are coordinated to antimony atoms *trans* to S(1) which is subsequently coordinated to tungsten. One of the major results is the different sequence of Sb–S bonds within the Sb_2S_2 ring, *i.e.* alternating short and long bonds in *cyclo*-[{2-(Me_2NCH_2)C_6H_4}SbS]$_2$[$W(CO)_5$], while in **11** the S(1) atom is involved in longer bonds [Sb(1)–S(1) 2.5523(9) Å; Sb(2)–S(1) 2.5594(9) Å] than the S(2) atom [Sb(1)–S(2) 2.4436(9) Å; Sb(2)–S(2) 2.4514(9) Å]. It should also be noted that the central four-membered Sb_2S_2 ring is slightly folded [fold angles: S(1)Sb(1)S(2)/S(1)Sb(2)S(2) 6.9, Sb(1)S(1)Sb(2)/Sb(1)S(2)Sb(2) 7.1°]

Table 3 Selected bond distances (Å) and angles (°) for **11**·0.25CH_3OH

Sb(1)–C(1)	2.155(3)	Sb(2)–C(20)	2.173(3)
Sb(1)–S(1)	2.5523(9)	Sb(2)–S(1)	2.5594(9)
Sb(1)–S(2)	2.4436(9)	Sb(2)–S(2)	2.4514(9)
Sb(1)–N(1)	2.529(3)	Sb(2)–N(1)	2.470(3)
N(1)–C(7)	1.280(5)	N(2)–C(26)	1.273(5)
N(1)–C(8)	1.443(4)	N(2)–C(27)	1.437(5)
W(1)–S(1)	2.6005(9)		
W(1)–C(39)	2.036(4)	C(39)–O(1)	1.148(5)
W(1)–C(40)	2.056(4)	C(40)–O(2)	1.136(5)
W(1)–C(41)	2.039(4)	C(41)–O(3)	1.148(5)
W(1)–C(42)	2.051(4)	C(42)–O(4)	1.141(5)
W(1)–C(43)	1.955(4)	C(43)–O(5)	1.159(5)
C(1)–Sb(1)–S(1)	94.11(10)	C(20)–Sb(2)–S(1)	92.85(9)
C(1)–Sb(1)–S(2)	96.00(10)	C(20)–Sb(2)–S(2)	102.25(8)
S(1)–Sb(1)–S(2)	88.78(3)	S(1)–Sb(2)–S(2)	88.45(3)
N(1)–Sb(1)–C(1)	73.58(12)	N(2)–Sb(2)–C(20)	73.47(11)
N(1)–Sb(1)–S(1)	166.13(7)	N(2)–Sb(2)–S(1)	160.64(7)
N(1)–Sb(1)–S(2)	86.23(6)	N(2)–Sb(2)–S(2)	81.39(7)
Sb(1)–S(1)–Sb(2)	88.64(3)	Sb(1)–S(2)–Sb(2)	93.70(3)
C(7)–N(1)–C(8)	119.5(3)	C(26)–N(2)–C(27)	120.8(3)
Sb(1)–N(1)–C(7)	107.1(2)	Sb(2)–N(2)–C(26)	110.1(2)
Sb(1)–N(1)–C(8)	126.3(2)	Sb(2)–N(2)–C(27)	127.9(2)
Sb(1)–S(1)–W(1)	101.99(3)	Sb(2)–S(1)–W(1)	102.76(3)
S(1)–W(1)–C(39)	92.82(12)	S(1)–W(1)–C(42)	91.01(12)
S(1)–W(1)–C(40)	92.84(11)	S(1)–W(1)–C(43)	177.63(12)
S(1)–W(1)–C(41)	91.14(11)		
C(39)–W(1)–C(40)	90.68(14)	C(40)–W(1)–C(42)	175.06(16)
C(39)–W(1)–C(41)	175.68(16)	C(40)–W(1)–C(43)	85.78(14)
C(39)–W(1)–C(42)	92.22(16)	C(41)–W(1)–C(42)	85.96(14)
C(39)–W(1)–C(43)	85.28(16)	C(41)–W(1)–C(43)	90.81(16)
C(40)–W(1)–C(41)	90.86(12)	C(42)–W(1)–C(43)	90.48(15)

and the endocyclic angles at sulfur atoms are significantly different (Table 3).

The *all-cis* orientation of the Sb–C and Sb–N bonds with respect to the Sb_2S_2 ring is most likely a consequence of the steric strain due to the bulky substituents on nitrogen. This also explains the presence of exclusively *all-trans* and *all-cis* isomers in the chloroform solution of **10** (see the above discussion of the NMR spectra).

Intramolecular S···H contacts, which involve the hydrogen atom in the *ortho* position of the aryl ring bound to antimony, are established in the molecules of all sulfides described here. The heterocyclic species **9** and **10** show further intramolecular $S\cdots H_{alkyl}$ contacts [$S(1)\cdots H(14C')_{methyl}$ 2.87 Å for **9**; $S(1)\cdots H(17')_{methine}$ 2.95 Å for **10**]. For the molecule of the sulfide **5** additional intramolecular C–H···π ($Ph_{centroid}$) contacts are present [$C(5)–H(5)_{aryl}\cdots Ph_{centroid}${C(27′)–C(32′)} 2.71 Å, γ = 6.4°; $C(17)–H(17)_{methine}\cdots Ph_{centroid}${C(20′)–C(25′)} 2.85 Å, γ = 16.0°].

Although no intermolecular interactions between heavy atoms were found in the crystals of **5**, **9**·CH_2Cl_2, **10** and **11**·0.25CH_3OH, a closer inspection revealed supramolecular architectures based on sulfur–hydrogen or C–H···π ($Ph_{centroid}$) contacts.[23] Thus, in the crystal of **5** layers of (C_{Sb},C_{Sb})- and (A_{Sb}, A_{Sb})-**5** isomers, respectively, are formed through intermolecular C–

H···π ($Ph_{centroid}$) interactions [C(11)–H(11)$_{aryl}$···$Ph_{centroid}$\{C(27′c)–C(32′c)\} 2.92 Å, γ = 15.7°], but no further contacts between alternating parallel layers are established (for details, see ESI†).

For the heterocyclic species **9**·CH_2Cl_2 and **10** different supramolecular arrangements are established in the crystal. Polymer chains of (A_{Sb},$C_{Sb'}$)-**9** isomers are formed based on weak sulfur–hydrogen contacts [S(1)···H(14Ba)$_{methyl}$ 3.00 Å] with no further contacts between parallel chains. Similarly a chain polymer of (C_{Sb},$A_{Sb'}$)-**10** is formed based on C–H···π ($Ph_{centroid}$) contacts [C(4)–H(4)$_{aryl}$···$Ph_{centroid}$\{C(8b)–C(13b)\} 2.73 Å, γ = 11.2°]. Further contacts of the same type connect parallel chains into layers [C(19)–H(19C)$_{methyl}$···$Ph_{centroid}$-\{C(8′d)–C(13′d)\} 2.81 Å, γ = 3.2°] and parallel layers into a 3D architecture, respectively [C(15)–H(15A)$_{methyl}$···$Ph_{centroid}$\{C(1′e)–C(6′e)\} 2.77 Å, γ = 11.8°] (for details, see ESI†).

Dimer associations are formed in the crystal of **11**·0.25CH_3OH through weak sulfur–hydrogen [S(2)···H(4′)$_{aryl}$ 3.02 Å] and quite strong C–H···π ($Ph_{centroid}$) contacts [C(3)–H(3)$_{aryl}$···$Ph_{centroid}$\{C(20′)–C(25′)\} 2.82 Å, γ = 6.1°]. Further weak O···H [O(1)···H(12′a)$_{aryl}$ 2.56 Å, O(5)···H(26b)$_{imine}$ 2.49 Å] contacts and strong C–H···π ($Ph_{centroid}$) [C(18)–H(18B)$_{methyl}$···$Ph_{centroid}$-\{C(8′a)–C(13′a)\} 2.59 Å, γ = 5.3°] connect the dimers into a polymer (for details, see ESI†).

Theoretical calculations

Theoretical calculations using DFT methods (see the Experimental section for further details) were carried out in order to investigate the geometrical isomers of the dimer associations of **7** and the geometrical isomers of **10**. Comparison of selected calculated and determined bond lengths and angles are provided in ESI, Tables S1 and S2.† A visual comparison of the calculated and determined structures is shown in ESI, Fig. S26 and S27.†

The calculated geometries reproduced to a great extent the structures determined by single crystal X-ray diffraction analysis. In the case of the *all-trans* dimer association of **7** a difference larger than 10% was found for the Br(1′)–Sb(1) bond lengths. This suggests that the intermolecular bonds strength at this level of theory was overestimated. The length of the Sb–N bond was also overestimated by 5.9%, and consequently the Br–Sb bond *trans* to N was elongated by the same amount. The bonding angles around antimony were slightly better described than the bond lengths. The largest difference, of 5.9%, was found for the C(1)–Sb(1)–Br(2) bond angle.

The calculated and determined bond lengths for the *all-trans* isomer of the sulfide **10** are in better agreement than in the dimer association of the dibromide **7**. For the *all-trans*-**10** isomer the largest differences, of 3.8 and 3.9%, were found for two of the Sb–S bond lengths. The calculated C–Sb–S angles were 3.9% larger than those determined.

Theoretical calculations reveal that the coordination of the nitrogen atom to the antimony brings a stabilization of 45.2 kJ mol^{-1} in **7** and of 76.7 kJ mol^{-1} in the monomer of **10**. The dimerization energy of **7**, considering the formation of the *all-trans* isomer, was found to be 80.1 kJ mol^{-1}. Dissociation of the *all-trans* isomer of **10** into monomers amounts to 152.4 kJ mol^{-1}. The calculated relative energy differences between geometrical isomers of the dimer association of **7** and between the isomers of **10**, respectively, are very small. The isomers found to have the lowest energy by theoretical calculations are different from those found in the crystals. This is most likely a result of packing forces in the solid state. The energies of the *trans*-Sb–C/*cis*-Sb–N, *all-trans*, and *all-cis* isomers of **7** are larger than the energy of the *cis*-Sb–C/*trans*-Sb–N isomer with 1.1, 4, and 8.5 kJ mol^{-1}, respectively. For **10** the theoretical data show the *trans*-Sb–C/*cis*-Sb–N isomer as being the most stable one. The energies of the *all-trans*, *cis*-Sb–C/*trans*-Sb–N, and *all-cis* isomers of **10** are with 1.8, 4.9, and 6.8 kJ mol^{-1} larger.

Conclusions

The rigidity induced by the presence of the C=N bond in the pendant arm and the sterically demanding group attached to nitrogen in (imino)aryl ligands of the type 2-(RN=CH)C_6H_4 (R = 2′,4′,6′-$Me_3C_6H_2$, 2′,6′-$^iPr_2C_6H_3$) were expected to influence significantly the solution behaviour and hence the structure of the corresponding organoantimony compounds. The chemistry of the title organoantimony species containing [2-(RN=CH)C_6H_4]$_n$Sb (n = 1, 2) fragments seems to parallel generally the results obtained with the wider investigated, more flexible 2-(Me_2NCH_2)C_6H_4 group. However, some important differences related to the bulkiness of the organic group attached to nitrogen were observed: (i) room temperature NMR spectra in $CDCl_3$ evidence equivalence of the organic groups at antimony for [2-(2′,4′,6′-$Me_3C_6H_2$N=CH)C_6H_4]$_2$SbBr (**3**), while for [2-(2′,6′-$^iPr_2C_6H_3$N=CH)C_6H_4]$_2$SbBr (**4**) the NMR data indicate not only the non-equivalence of the organic ligands (as was also observed in the solid state), but also the restriction of the free rotation of one of the bulky 2,6-$^iPr_2C_6H_3$ groups around the C–N(=C) single bond; (ii) the steric stress prevents the intramolecular coordination of both N(sp^2) to an antimony atom in the dinuclear sulfide [\{2-(2′,6′-$^iPr_2C_6H_3$N=CH)C_6H_4\}$_2$-Sb]$_2$S (**5**); (iii) in the complex *cyclo*-[\{2-(2′,6′-$^iPr_2C_6H_3$N=CH)-C_6H_4\}SbS]$_2$[W(CO)$_5$] (**11**) the W(CO)$_5$ fragment is coordinated to the sulfur atom of the *all-cis* isomer of the sulfide **10**, while in the related *cyclo*-[\{2-(Me_2NCH_2)C_6H_4\}SbS]$_2$[W(CO)$_5$] the same metal carbonyl unit is coordinated to the *cis*-Sb–C/*trans*-Sb–N isomer of the heterocyclic sulfide. Theoretical calculations reveal that in the gas phase the energy difference between the geometrical isomers of the dimer associations of **7** and those between the geometrical isomers of **10** are small (<9 kJ mol^{-1}). Most likely, several isomers are present in solution and the packing forces play an important role in the crystallization process.

Experimental section

General procedures

Multinuclear NMR spectra (^{1}H, ^{13}C) were recorded at room temperature on a Bruker Avance 300 (**1**, **2**, **4**, **5**, **9**, **10**, **11**) and a

Bruker Avance III 500 (**3**, **6**, **7**, **8**) instrument. The ^{1}H chemical shifts are reported in δ units (ppm) relative to the residual peak of the deuterated solvent (ref. $CDCl_3$: ^{1}H 7.26 ppm; DMSO-d_5: ^{1}H 2.50 ppm). The ^{13}C chemical shifts are reported in δ units (ppm) relative to the peak of the solvent (ref. $CDCl_3$: ^{13}C 77.0 ppm; DMSO-d_6: ^{13}C 39.43 ppm). ^{1}H and ^{13}C resonances were assigned using 2D NMR experiments (COSY, HMQC and HMBC). The NMR spectra were processed using the *MestReC* and *MestReNova* software.[25] Mass spectra were recorded with a Finnigan MAT 8200 (EI) and an Applied Biosystems (Type Mariner) (ESI/APCI-TOF) instrument. Infrared spectra were recorded on a BioRad FTS-165 spectrometer, using ATR-IR. Melting points were measured with an Electrothermal 9200 apparatus and are not corrected. Elemental analyses were carried out with a Perkin-Elmer 2400 and a CHN-Analysator Type FlashAE 1112 (Co. Thermo) instrument. All manipulations were carried out under an inert atmosphere of argon using Schlenk techniques. Solvents were dried and freshly distilled under argon prior to use. Starting materials such as 2-($BrCH_2$)C_6H_4Br, 2′,4′,6′-$Me_3C_6H_2NH_2$, 2′,6′-$^{i}Pr_2C_6H_3NH_2$, $SbCl_3$, KBr, KOH, $Na_2S{\cdot}9H_2O$ or $W(CO)_6$ were obtained from Aldrich or Merck, and were used as received.

Synthesis of 2-(2′,4′,6′-$Me_3C_6H_2N{=}CH)C_6H_4Br$ (1)

2-Bromobenzaldehyde (35.00 g, d = 1.585 g cm^{-3}, 22.1 mL, 0.19 mol) and 2,4,6-trimethylaniline (25.50 g, d = 0. 963 g cm^{-3}, 26.5 mL, 0.19 mol) were dissolved in toluene (100 mL) in a round bottom flask. The reaction mixture was heated at reflux for 8 h using a Dean–Stark apparatus to remove the water. Then the reaction mixture was cooled to room temperature and the solvent was removed using a rotary evaporator to give a brown oil which solidified at 0 °C. This solid was recrystallized from hexane to give the title compound as a yellow material (49.0 g, 85%), mp 51–52 °C. Anal. calcd for $C_{16}H_{16}BrN$ (302.21): C, 63.59; H, 5.34; N, 4.63; Found: C, 63.26; H, 5.16; N, 4.26%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.16 (6 H, s, H-7′, CH_3), 2.30 (3 H, s, H-8′, CH_3), 6.92 (2 H, s, H-3′, C_6H_3), 7.34 (1 H, ddd, H-5, C_6H_4, $^{3}J_{HH}$ = 7.4, $^{4}J_{HH}$ = 1.9 Hz), 7.44 (1 H, dd, H-4, C_6H_4, $^{3}J_{HH}$ = 7.3 Hz), 7.63 (1 H, dd, H-6, C_6H_4, $^{3}J_{HH}$ = 8.0, $^{4}J_{HH}$ = 1.2 Hz), 8.27 (1 H, dd, H-3, C_6H_4, $^{3}J_{HH}$ = 7.7, $^{4}J_{HH}$ = 1.8 Hz), 8.62 (1 H, s, H-7, C*H*═N). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 18.30 (s, C-7′, CH_3), 20.73 (s, C-8′, CH_3), 125.67 (s, C-2), 127.01 (s, C-2′), 127.71 (s, C-4), 128.63 (s, C-3), 128.78 (s, C-3′), 132.32 (s, C-5), 133.12 (s, C-6), 133.33 (s, C-4′), 134.68 (s, C-1), 148.42 (s, C-1′), 162.16 (s, C-7, *C*H═N). MS (EI, 70 eV, 200 °C), m/z (%): 301 (70) [M^+], 222 (20) [M^+ − Br], 146 (100) [M^+ − C_6H_5Br]. IR: ν(CH═N) 1628 (vs) cm^{-1}.

Synthesis of 2-(2′,6′-$^{i}Pr_2C_6H_3N{=}CH)C_6H_4Br$ (2)

Compound **2** was prepared as described above for **1** from 2-bromobenzaldehyde (27.00 g, d = 1.585 g cm^{-3}, 17.0 mL, 0.15 mol) and 2,6-diisopropylaniline (25.83 g, d = 0.94 g cm^{-3}, 27.5 mL, 0.15 mol), in toluene (100 mL). After removal of the solvent using a rotary evaporator the remaining brown oil solidified at 0 °C. Recrystallization from hexane gave **2** as a yellow material (39 g, 76%), mp 74–76 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.21 (12 H, d, H-8′, CH_3, $^{3}J_{HH}$ 6.9 Hz), 2.98 (2 H, hept, H-7′, CH, $^{3}J_{HH}$ 6.8 Hz), 7.16 (3 H, m, H-3′,4′, C_6H_3), 7.37 (1 H, ddd, H-5, C_6H_4, $^{3}J_{HH}$ = 7.7, $^{4}J_{HH}$ = 1.4 Hz), 7.46 (1 H, dd, H-4, C_6H_4, $^{3}J_{HH}$ = 7.5 Hz), 7.65 (1 H, d, H-6, C_6H_4, $^{3}J_{HH}$ = 7.7 Hz), 8.27 (1 H, dd, H-3, C_6H_4, $^{3}J_{HH}$ = 7.7, $^{4}J_{HH}$ = 1.3 Hz), 8.59 (1 H, s, H-7, C*H*═N). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 23.55 (s, C-8′, CH_3), 27.94 (s, C-7′, CH), 123.07 (s, C-3′), 124.39 (s, C-4′), 125.73 (s, C-1), 127.79 (s, C-4), 128.82 (s, C-3), 132.43 (s, C-5), 133.21 (s, C-6), 134.57 (s, C-2), 137.59 (s, C-2′), 148.90 (s, C-1′), 161.48 (s, C-7, *C*H═N). MS (EI, 70 eV, 200 °C), m/z (%): 343 (100) [M^+], 328 (85) [M^+ − CH_3], 188 (30) [M^+ − C_6H_5Br]. IR: ν(CH═N) 1624 (vs) cm^{-1}.

Synthesis of [2-(2′,4′,6′-$Me_3C_6H_2N{=}CH)C_6H_4]_2SbBr$ (3)

A solution of **1** (2.00 g, 6.62 mmol) in THF (70 mL) was added dropwise, under stirring, to magnesium filings (0.17 g, 7.08 mmol, 7% excess) activated with 1,2-dibromoethane (0.5 mL). The addition was completed after 0.5 h and the brown reaction mixture was stirred for a further 1.5 h under reflux. Then it was cooled to room temperature and the unreacted Mg was separated. The Grignard solution was added dropwise to a solution of $SbCl_3$ (0.75 g, 3.30 mmol) in THF (20 mL) at −78 °C and the reaction mixture was stirred at this temperature for 1 h, then for 12 h at room temperature. The solvent was removed under vacuum and the oily residue was washed with diethyl ether and hexane, resulting in a yellow solid which was filtered off and dried under vacuum (0.80 g, 38%), mp 249–251 °C. Anal. calcd for $C_{32}H_{32}BrN_2Sb$ (646.27): C, 59.47; H, 4.99; N, 4.33; Found: C, 59.13; H, 5.10; N, 4.17%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.65 (12 H, s, H-7′, CH_3), 2.20 (6 H, s, H-8′, CH_3), 6.70 (4 H, s, H-3′, C_6H_3), 7.20 (2 H, ddd, H-4, C_6H_4, $^{3}J_{HH}$ = 7.4, $^{4}J_{HH}$ = 0.9 Hz), 7.35 (2 H, d, H-3, C_6H_4, $^{3}J_{HH}$ = 7.3 Hz), 7.40 (2 H, ddd, H-5, C_6H_4, $^{3}J_{HH}$ = 7.5, $^{4}J_{HH}$ = 0.8 Hz), 7.68 (2 H, d, H-6, C_6H_4, $^{3}J_{HH}$ = 7.4 Hz), 8.29 (2 H, s, H-7, C*H*═N). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 17.75 (s, C-7′, CH_3), 20.63 (s, C-8′, CH_3), 127.40 (s, C-2′), 127.65 (s, C-5), 128.24 (s, C-3′), 130.70 (s, C-4), 131.53 (s, C-6), 132.49 (s, C-4′), 138.25 (s, C-3), 140.79 (s, C-1), 147.78 (s, C-1′), 148.45 (s, C-2), 164.34 (s, C-7, C*H*═N). MS (ESI+), m/z (%): 565 (100) [R_2Sb^+] [R = 2-(2′,4′,6′-$Me_3C_6H_2N{=}CH)C_6H_4$]. IR: ν(CH═N) 1624 (vs) cm^{-1}.

Synthesis of [2-(2′,6′-$^{i}Pr_2C_6H_3N{=}CH)C_6H_4]_2SbBr$ (4)

A solution of **2** (2.00 g, 5.81 mmol) in THF (70 mL) was added dropwise during 0.5 h, under stirring, to magnesium filings (0.15 g, 6.25 mmol, 7.5% excess), activated with 1,2-dibromoethane (0.5 mL). The brown reaction mixture was stirred for an additional 1.5 h under reflux, then cooled to room temperature and the unreacted Mg was separated. The Grignard solution was added dropwise to a solution of $SbCl_3$ (0.64 g, 2.89 mmol) in THF (20 mL), at −78 °C, and the reaction mixture was stirred at this temperature for 1 h, then for 12 h at room temperature. The solvent was removed under vacuum and the oily residue was washed with hexane and ethanol until a yellow precipitate deposited. The solid was filtered off, dried under vacuum, then dissolved in CH_2Cl_2 (40 mL) and the solution was treated with an aqueous solution of KBr (0.59 g, 4.96 mmol) at room temperature. The reaction mixture was

stirred for 12 h. The organic layer was separated, the aqueous layer was washed with CH_2Cl_2 (3 × 10 mL) and the unified organic phases were dried over $MgSO_4$. Evaporation of the solution under vacuum yielded **4** as a yellow solid (0.90 g, 43%), mp 225–226 °C. Anal. calcd for $C_{38}H_{44}BrN_2Sb$ (730.43): C, 62.49; H, 6.07; N, 3.84; Found: C, 62.30; H, 6.07; N, 3.76%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.46 [3 H, d, H-8′$_{a1}$, CH_3 (A), $^3J_{HH}$ 6.5 Hz], 0.78 [3 H, d, H-8′$_{a2}$, CH_3 (A), $^3J_{HH}$ 6.5 Hz], 0.95 [6 H, d, H-8′$_1$, CH_3 (B), $^3J_{HH}$ 6.5 Hz], 1.06 [12 H, m, H-8′$_{b1}$ (A) + H-8′$_{b2}$ (A) + H-8′$_2$ (B), CH_3], 1.81 [1 H, hept, H-7′$_a$, CH (A), $^3J_{HH}$ 6.5 Hz], 2.85 [3 H, m, H-7′$_b$ (A) + H-7′ (B), CH], 7.02–7.30 [8 H, m, H-5,6, C_6H_4 (B) + H-3′$_a$,3′$_b$,4′ (A) + H-3′,4′ (B), C_6H_3], 7.45 [1 H, dd, H-4, C_6H_4 (B), $^3J_{HH}$ = 6.2 Hz], 7.59 [1 H, d, H-3, C_6H_4 (B), $^3J_{HH}$ = 7.2 Hz], 7.71 [1 H, dd, H-4, C_6H_4 (A), $^3J_{HH}$ = 7.1 Hz], 7.80 [1 H, dd, H-5, C_6H_4 (A), $^3J_{HH}$ = 7.1 Hz], 7.87 [1 H, d, H-3, C_6H_4 (A), $^3J_{HH}$ = 7.0 Hz], 8.36 [1 H, s, H-7, CH═N (B)], 8.43 [1 H, s, H-7, CH═N (A)], 8.99 [1 H, d, H-6, C_6H_4 (A), $^3J_{HH}$ = 7.0 Hz]. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 22.09 [s, C-8′$_{a1}$, CH_3 (A)], 23.97 [s, H-8′$_{b1}$ (A) + H-8′$_1$ (B), CH_3], 24.59 [s, H-8′$_2$, CH_3 (B)], 24.80 [s, C-8′$_{b2}$, CH_3 (A)], 25.08 [s, C-8′$_{a2}$, CH_3 (A)], 27.77 [s, C-7′, CH (B)], 28.00 [s, C-7′$_a$, CH (A)], 28.48 [s, C-7′$_b$, CH (A)], 122.89 [s, C-3′ (B)], 123.23 [s, C-3′$_a$ (A)], 123.86 [s, C-3′$_b$ (A)], 124.25 [s, C-4′ (B)], 126.89 [s, C-4′ (A)], 129.22 [s, C-4 (A)], 129.51 [s, C-4 (B)], 131.82 [s, C-5 (B)], 132.82 [s, C-3 (A)], 133.19 [s, C-3 (B)], 133.43 [s, C-5 (A)], 135.55 [s, C-6 (B)], 138.53 [s, C-2′ (B)], 139.86 [s, C-2,6 + C-2′$_b$ (A)], 140.42 [s, C-2′$_a$ (A)], 143.64 [s, C-1′ (A)], 145.59 [s, C-1 (B)], 148.26 [s, C-2, C-1′ (B)], 153.28 [s, C-1 (A)], 164.87 [s, C-7, CH═N (B)], 169.66 [s, C-7, CH═N (A)]. MS (ESI+), *m*/*z* (%): 809 (40) [$R_2SbBr_2^+$], 649 (100) [R_2Sb^+] [R = 2-(2′,6′-^{i}Pr$_2$C$_6$H$_3$N═CH)C$_6$H$_4$]. IR: ν(CH═N) 1634 (m) cm^{-1}.

Synthesis of [{2-(2′,6′-^{i}Pr$_2$C$_6$H$_3$N═CH)C$_6$H$_4$}$_2$Sb]$_2$S (5)

A solution of $Na_2S{\cdot}9H_2O$ (0.04 g, 0.16 mmol, 70% excess) in water (10 mL) was added to a solution of **4** (0.15 g, 0.21 mmol) in toluene (30 mL). The reaction mixture was stirred for 2 days at room temperature, then the yellow organic phase was separated and the water solution was washed with CH_2Cl_2 (2 × 30 mL). The unified organic phases were dried over anhydrous Na_2SO_4. Removal of the solvent under vacuum gave **5** as a yellow solid (0.12 g, 86%), mp 247–249 °C. Anal. calcd for $C_{76}H_{88}N_4SSb_2$ (1333.12): C, 68.47; H, 6.65; N, 4.20; Found: C, 68.92; H, 6.62; N, 4.20%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.83 (48 H, s,br, H-8′, CH_3), 2.59 (8 H, s,br, H-7′, CH), 6.73 (4 H, s,br, H-4, C_6H_4), 7.06 (12 H, m, H-3′,4′, C_6H_3), 7.24 (8 H, m, H-3,5, C_6H_4), 7.62 (4 H, d, H-6, C_6H_4, $^3J_{HH}$ = 7.2 Hz), 8.34 (4 H, s,br, H-7, CH═N). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 23.72, 24.10 (s, C-8′, CH_3), 27.75 (s, C-7′, CH), 122.93 (s, C-3′), 124.45 (s, C-4′), 128.16 (s, C-3,5), 131.22 (s, C-6), 131.49 (s, C-4), 137.33 (s, C-2), 138.65 (s, C-2′), 139.14 (s, C-1), 146.76 (s, C-1′), 164.96 (s, C-7, CH═N). MS (ESI+), *m*/*z* (%): 1329 (4) [$M^+ - H$], 649 (100) [R_2Sb^+] [R = 2-(2′,6′-^{i}Pr$_2$C$_6$H$_3$N═CH)C$_6$H$_4$]. IR: ν(CH═N) 1626 (m) cm^{-1}.

Synthesis of [2-(2′,4′,6′-Me$_3$C$_6$H$_2$N═CH)C$_6$H$_4$]SbBr$_2$ (6)

A solution of **1** (2.00 g, 6.62 mmol) in THF (90 mL) was added dropwise, under stirring, to magnesium filings (0.175 g, 7.28 mmol, 10% excess), activated with 1,2-dibromoethane (0.5 mL). The addition was completed after 0.5 h and the brown reaction mixture was stirred for a further 2 h under reflux. Then it was cooled to room temperature and the unreacted Mg was separated. The Grignard solution was added dropwise to a solution of $SbCl_3$ (1.51 g, 6.62 mmol) in THF (20 mL), at −78 °C, and the reaction mixture was stirred at this temperature for 1 h, then for 12 h at room temperature. The solvent was removed under vacuum and the oily residue was washed with hexane and ethanol, when a yellow solid deposited. The solid was filtered off, dried under vacuum, then dissolved in CH_2Cl_2 (40 mL) and the solution was treated with an aqueous solution of KBr (1.89 g, 15.88 mmol) at room temperature. The reaction mixture was stirred for 12 h. The organic layer was separated, the aqueous layer was washed with CH_2Cl_2 (3 × 10 mL) and the unified organic phase was dried over $MgSO_4$. Evaporation of the solution under vacuum yielded **6** as a yellow solid (1.22 g, 37%), mp 229–230 °C. Anal. calcd for $C_{16}H_{16}Br_2NSb$ (503.87): C, 38.14; H, 3.20; N, 2.78; Found: C, 38.54; H, 3.65; N, 2.49%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.24 (6 H, s, H-7′, CH_3), 2.32 (3 H, s, H-8′, CH_3), 6.96 (2 H, s, H-3′, C_6H_3), 7.68 (1 H, ddd, H-4, C_6H_4, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.2 Hz), 7.80 (1 H, ddd, H-5, C_6H_4, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.3 Hz), 7.81 (1 H, dd, H-3, C_6H_4, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.3 Hz), 8.54 (1 H, s, H-7, C*H*═N), 8.84 (1 H, d, H-6, C_6H_4, $^3J_{HH}$ = 7.8 Hz). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 18.96 (s, C-7′, CH_3), 20.81 (s, C-8′, CH_3), 129.33 (s, C-1), 129.56 (s, C-3′, C-2′), 131.14 (s, C-4), 132.69 (s, C-3), 134.10 (s, C-5), 136.51 (s, C-6), 136.84 (s, C-4′), 138.69 (s, C-2), 142.14 (s, C-1′), 169.90 (s, C-7, C*H*═N). MS (ESI+), *m*/*z* (%): 424 (100) [$RSbBr^+$] [R = 2-(2′,4′,6′-Me$_3$C$_6$H$_2$N═CH)C$_6$H$_4$]. IR: ν(CH═N) 1617 (s) cm^{-1}.

Synthesis of [2-(2′,6′-^{i}Pr$_2$C$_6$H$_3$N═CH)C$_6$H$_4$]SbBr$_2$ (7)

A solution of **2** (3.00 g, 8.71 mmol) in THF (70 mL) was added dropwise, under stirring, to magnesium filings (0.25 g, 10.04 mmol, 15% excess), activated with 1,2-dibromoethane (0.5 mL). The addition was completed after 0.5 h, the brown reaction mixture was stirred for an additional 2 h under reflux, then cooled to room temperature and the unreacted Mg was separated. The Grignard solution was added dropwise to a solution of $SbCl_3$ (1.99 g, 8.72 mmol) in THF (20 mL), at −78 °C, and the reaction mixture was stirred at this temperature for 1 h, then for 12 h at room temperature. The solvent was removed under vacuum and the oily residue was washed with hexane, when a yellow precipitate deposited. The solid was filtered off, dried under vacuum, then dissolved in CH_2Cl_2 (40 mL) and the solution was treated with an aqueous solution of KBr (1.30 g, 10.92 mmol) at room temperature. The reaction mixture was stirred for 12 h. The organic layer was separated, the aqueous layer was washed with CH_2Cl_2 (3 × 10 mL) and the unified organic phases were dried over $MgSO_4$. Evaporation of the solution under vacuum afforded **7** as a yellow solid (2.50 g, 53%), mp 234–237 °C. Anal. calcd for $C_{19}H_{422}Br_2NSb$ (545.95): C, 41.80; H, 4.06; N, 2.57; Found: C, 41.81; H, 3.95; N, 2.50%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.16 (6 H, d, H-8′$_1$, CH_3, $^3J_{HH}$ 6.8 Hz), 1.28 (6 H, d, H-8′$_2$, CH_3, $^3J_{HH}$ 6.7 Hz), 2.98 (2 H, hept,

H-7′, CH, $^3J_{HH}$ 6.8 Hz), 7.28 (3 H, m, H-3′,4′, C_6H_3), 7.70 (1 H, dd, H-4, C_6H_4, $^3J_{HH}$ = 7.5 Hz), 7.81 (2 H, m, H-3,5, C_6H_4), 8.48 (1 H, s, H-7, CH=N), 8.90 (1 H, d, H-6, C_6H_4, $^3J_{HH}$ = 6.7 Hz). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 23.93 (s, C-8′$_2$, CH_3), 25.63 (s, C-8′$_1$, CH_3), 28.84 (s, C-7′, CH), 124.19 (s, C-3′), 127.41 (s, C-4′), 131.16 (s, C-4), 132.92 (s, C-3), 134.20 (s, C-5), 137.93 (s, C-6), 138.45 (s, C-2), 140.58 (s, C-2′), 141.42 (s, C-1′), 149.38 (s, C-1), 169.15 (s, C-7, CH=N). MS (ESI+), *m*/*z* (%): 466 (100) [$RSbBr^+$] [R = 2-(2′,6′-^{i}Pr$_2$$C_6H_3N$=CH)$C_6H_4$]. IR: ν(CH=N) 1621 (s) cm^{-1}.

Synthesis of *cyclo*-[{2-(2′,6′-^{i}Pr$_2$$C_6H_3N$=CH)$C_6H_4$}SbO]$_3$ (8)

A solution of KOH (0.022 g, 0.39 mmol, 10% excess) in water (10 mL) was added to a solution of **7** (0.10 g, 0.18 mmol) in toluene (20 mL). The reaction mixture was stirred for 4 days at room temperature, then the organic layer was separated and the aqueous phase was washed with toluene (2 × 15 mL). The toluene solution was dried over $MgSO_4$, then filtered and the solvent was removed under vacuum. The resulting pale yellow clay was triturated with hexane to afford **8** as a colourless solid (0.06 g, 83%), mp 194–195 °C. Anal. calcd for $C_{57}H_{66}N_3O_3Sb_3$ (1206.42): C, 56.75; H, 5.51; N, 3.48; Found: C, 56.34; H, 5.50; N, 3.35%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.09 (36 H, m, H-8′, CH_3, *cis* + *trans*), 3.14 (6 H, m, H-7′, CH, *cis* + *trans*), 7.04 (2 H, ddd, H-5, C_6H_4, *cis*, $^3J_{HH}$ = 7.4, $^4J_{HH}$ = 1.0 Hz), 7.18 (6 H, m, H-3′,4′, C_6H_3, *cis*), 7.24 (3 H, m, H-3′,4′, C_6H_3, *trans*), 7.39 [4 H, m, (H-4, C_6H_4, *cis*) + (H-4,5, C_6H_4, *trans*)], 7.57 (1 H, dd, H-3, C_6H_4, *trans*, $^3J_{HH}$ = 7.2, $^4J_{HH}$ = 1.1 Hz), 7.60 (2 H, d, H-3, C_6H_4, *cis*, $^3J_{HH}$ = 7.2 Hz), 8.18 (2 H, d, H-6, C_6H_4, *cis*, $^3J_{HH}$ = 7.2 Hz), 8.35 (2 H, s, H-7, C*H*=N, *cis*), 8.36 (1 H, s, H-7, C*H*=N, *trans*), 8.50 (1 H, dd, H-6, C_6H_4, *trans*, $^3J_{HH}$ = 7.0, $^4J_{HH}$ = 1.4 Hz). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 24.33 (s,br, C-8′, CH_3, *cis* + *trans*), 27.90 (s, C-7′, CH, *cis*), 28.02 (s, C-7′, CH, *trans*), 123.25 (s, C-3′, *cis*), 123.43 (s, C-3′, *trans*), 125.11 (s, C-4′, *trans*), 125.16 (s, C-4′, *cis*), 128.83 (s, C-4, *cis*), 128.88 (s, C-4, *trans*), 131.62 (s, C-5, *cis*), 131.82 (s, C-3, *cis*), 131.96 (s, C-5, *trans*), 132.08 (s, C-3, *trans*), 133.85 (s, C-6, *cis*), 133.96 (s, C-6, *trans*), 139.36 (s, C-2, *trans*), 139.50 (s, C-2′, *cis*), 139.56 (s, C-2′, *trans*), 139.59 (s, C-2, *cis*), 146.45 (s, C-1′, *cis*), 146.98 (s, C-1′, *trans*), 159.22 (s, C-1, *trans*), 159.97 (s, C-1, *cis*), 166.24 (s, C-7, CH=N, *cis*), 166.32 (s, C-7, CH=N, *trans*). MS (ESI+), *m*/*z* (%): 1206 (50) [M^+ + H], 805 (100) [$(RSbO)_2^+$ + H], 402 (48) [$RSbO^+$ + H] [R = 2-(2′,6′-^{i}Pr$_2$$C_6H_3N$=CH)$C_6H_4$]. IR: ν(CH=N) 1628 (vs) cm^{-1}.

Synthesis of *cyclo*-[{2-(2′,4′,6′-Me$_3$$C_6H_2N$=CH)$C_6H_4$}SbS]$_2$ (9)

A solution of $Na_2S{\cdot}9H_2O$ (0.06 g, 0.26 mmol) in water (10 mL) was added to a solution of **6** (0.13 g, 0.26 mmol) in toluene (15 mL). The reaction mixture was stirred for 2 h at room temperature, then the yellow organic phase was separated and the aqueous phase was washed with toluene (2 × 15 mL). The toluene solution was dried over anhydrous Na_2SO_4. Evaporation of the solution under vacuum afforded **9** as a yellow solid (0.07 g, 72%), mp 238–240 °C. Anal. calcd for $C_{32}H_{32}N_2S_2Sb_2$ (752.24): C, 51.09; H, 4.29; N, 3.72; Found: C, 51.17; H, 4.43; N, 3.51%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.13 (12 H, s, H-7′, CH_3, isomer **9a**), 2.18 (12 H, s, H-7′, CH_3, isomer **9b**), 2.28 (12 H, s, H-8′, CH_3, isomers **9a** + **9b**), 6.87 (8 H, s, H-3′, C_6H_3, **9a** + **9b**), 7.31 (2 H, dd, H-5, C_6H_4, $^3J_{HH}$ = 7.2 Hz, **9b**), 7.41 (2 H, dd, H-4, C_6H_4, $^3J_{HH}$ = 7.3 Hz, **9b**), 7.58 (2 H, dd, H-4, C_6H_4, $^3J_{HH}$ = 7.4 Hz, **9a**), 7.63 (2 H, d, H-3, C_6H_4, $^3J_{HH}$ = 7.4 Hz, **9b**), 7.73 (4 H, m, H-3,5, C_6H_4, **9a**), 8.346 (2 H, s, H-7, C*H*=N, **9b**), 8.353 (2 H, s, H-7, C*H*=N, **9a**), 8.54 (2 H, d, H-6, C_6H_4, $^3J_{HH}$ = 7.2 Hz, **9b**), 9.12 (2 H, d, H-6, C_6H_4, $^3J_{HH}$ = 7.5 Hz, **9a**); integral ratio 1.4 : 1 for isomers **9a** : **9b**. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 17.80 (s, C-7′, CH_3, isomer **9a**), 18.92 (s, C-7′, CH_3, isomer **9b**), 20.74 (s, C-8′, CH_3, isomers **9a** + **9b**), 128.45 (s, C-4, **9b**), 128.49 (s, C-2′, **9b**), 128.56 (s, C-3′, **9b**), 128.92 (s, C-3′, **9a**), 128.99 (s, C-2′, **9a**), 129.07 (s, C-4, **9a**), 131.12 (s, C-5, **9b**), 132.18 (s, C-3, **9b**), 132.24, 132.68 (s, C-3/C-5, **9a**), 134.63 (s, C-4′, **9a**), 134.70 (s, C-4′, **9b**), 136.01 (s, C-6, **9a**), 136.46 (s, C-6, **9b**), 138.70 (s, C-2, **9b**), 138.90 (s, C-2, **9a**), 144.99 (s, C-1′, **9b**), 145.32 (s, C-1′, **9a**), 152.48 (s, C-1, **9b**), 153.38 (s, C-1, **9a**), 167.01 (s, C-7, C*H*=N, **9b**), 167.32 (s, C-7, C*H*=N, **9a**). MS (EI, 70 eV, 200 °C), *m*/*z* (%): 752 (70) [M^+], 376 (6) [$RSbS^+$], 343 (100) [RSb^+] [R = 2-(2′,4′,6′-$Me_3C_6H_2N$=CH)C_6H_4]. IR: ν(CH=N) 1622 (vs) cm^{-1}.

Synthesis of *cyclo*-[{2-(2′,6′-^{i}Pr$_2$$C_6H_3N$=CH)$C_6H_4$}SbS]$_2$ (10)

A solution of $Na_2S{\cdot}9H_2O$ (0.06 g, 0.26 mmol) in water (10 mL) was added to a solution of **7** (0.10 g, 0.18 mmol) in toluene (30 mL). The reaction mixture was stirred for 2 h at room temperature, then the yellow organic phase was separated and the aqueous phase was washed with toluene (2 × 30 mL). The toluene solution was dried over anhydrous Na_2SO_4. Removal of the solvent under vacuum gave **10** as an orange solid (0.06 g, 80%), mp 276–278 °C. Anal. calcd for $C_{38}H_{44}N_2S_2Sb_2$ (836.40): C, 54.57; H, 5.30; N, 3.35; Found: C, 54.89; H, 5.48; N, 3.97%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.17 (48 H, s,br, H-8′, CH_3, isomers **10a** + **10b**), 3.06 (8 H, m, H-7′, CH, **10a** + **10b**), 7.22 (12 H, m, H-3′,4′, C_6H_3, **10a** + **10b**; 2H, m, H-5, C_6H_4, **10b**), 7.42 (2 H, dd, H-4, C_6H_4, $^3J_{HH}$ = 7.3 Hz, **10b**), 7.60 (2 H, dd, H-4, C_6H_4, $^3J_{HH}$ = 7.3 Hz, **10a**), 7.72 (4 H, m, H-3,5, C_6H_4, **10a**; 2 H, m, H-3, C_6H_4, **10b**), 8.35 (4 H, m, H-7, CH=N, **10a** + **10b**; 2 H, m, H-6, C_6H_4, **10b**), 9.09 (2 H, d, H-6, C_6H_4, $^3J_{HH}$ = 7.2 Hz, **10a**); integral ratio 1.8 : 1 for isomers **10a** : **10b**. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 23.80, 25.30 (s,br, C-8′, CH_3, isomers **10a** + **10b**), 28.26 (s, C-7′, CH, **10a**), 28.29 (s, C-7′, CH, **10b**), 123.58, 123.64, 125.89 (s, C-3′,4′, **10a** + **10b**; C-5, **10b**), 128.40 (s, C-4, **10b**), 129.15 (s, C-4, **10a**), 132.35 (s, C-3, **10b**), 132.48, 132.87 (s, C-3,5, **10a**), 135.96 (s, C-6, **10a**), 136.93 (s, C-6, **10b**), 138.54 (s, C-2, **10b**), 138.78 (s, C-2, **10a**), 139.74 (s, C-1′, **10a** + **10b**), 139.99 (s, C-2′, **10a** + **10b**), 144.71 (s, C-1, **10b**), 153.77 (s, C-1, **10a**), 166.45 (s, C-7, CH=N, **10b**), 166.74 (s, C-7, CH=N, **10a**). MS (ESI+), *m*/*z* (%): 837 (100) [M^+ + H] [R = 2-(2′,6′-^{i}Pr$_2$$C_6H_3N$=CH)$C_6H_4$]. IR: ν(CH=N) 1619 (s) cm^{-1}.

Synthesis of *cyclo*-[{2-(2′,6′-^{i}Pr$_2$$C_6H_3N$=CH)$C_6H_4$}SbS]$_2$-[W(CO)$_5$] (11)

A solution of [W(CO)$_5$(thf)] [prepared from W(CO)$_6$ (0.09 g, 0.24 mmol) by irradiation with a UV lamp, in THF (200 mL)] was added to **10** (0.20 g, 0.24 mmol) in THF (10 mL) and the mixture was stirred for 12 h at room temperature. After removal of the solvent under vacuum, the remaining yellow-

brown product was washed with hexane (35 mL) to give **11** as an orange-brown solid (0.18 g, 65%), mp 279–283 °C. Anal. calcd for $C_{43}H_{44}N_2O_5S_2Sb_2W$ (1160.30): C, 44.51; H, 3.82; N, 2.41; Found: C, 44.74; H, 3.92; N, 2.28%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.20 (24 H, m,br, H-8′, CH_3), 2.94 (4 H, s,br, H-7′, CH), 7.19 (6 H, s,br, H-3′,4′, C_6H_3), 7.49 (4 H, m,br, H-4,5, C_6H_4), 7.70 (2 H, m,br, H-3, C_6H_4), 8.39 (2 H, s, H-7, CH═N), 8.57 (2 H, m,br, H-6, C_6H_4). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 23.61, 24.07, 25.10, 25.69 (s,br, C-8′, CH_3), 28.26, 28.98 (s,br, C-7′, CH), 123.88 (s,br, C-3′), 126.66 (s, C-4′), 129.57 (s, C-4), 132.49, 132.63 (s, C-3,5), 136.58 (s, C-6), 138.46 (s, C-2), 138.94 (s, C-2′), 143.68 (s, C-1′), 153.83 (s, C-1), 168.03 (s, C-7, CH═N), 198.41 (s, *C*O-eq, $^1J_{WC}$ = 127.7 Hz), 200.30 (s, *C*O-ax). MS (ESI+), *m*/*z* (%): 1134 (100) [M^+ − CO], 1078 (83) [M^+ − 3CO], 748 (28) [M^+ − RSbS], 632 (33) [(RSbS)W(CO)$^+$] [R = 2-(2′,6′-^{i}Pr$_2$C$_6$H$_3$N═CH)C$_6$H$_4$]. IR: ν(CO) 2065 (s), 1974 (w), 1914 (vs), 1869 (vs); ν(CH═N) 1618 (m) cm^{-1}.

Crystal structures

Slow diffusion of *n*-hexane into CH_2Cl_2 solutions afforded the isolation of single crystals of **4** (4 : 1 v/v) or **5**, **7**, **9**·CH_2Cl_2 and **10** (3 : 1 v/v). Crystals of **11**·0.25CH_3OH were similarly grown using a *n*-hexane–CH_2Cl_2 mixture (3 : 1), which contained methanol (stabilizer present in the methylene chloride). Slow diffusion of *n*-hexane at ambient temperature into a $CHCl_3$ solution (4 : 1 v/v) resulted in crystals of **6**·$CHCl_3$. The details of the crystal structure determination and refinement are given in Tables 4 and 5. The crystals were mounted on cryo-loops (**4**, **9**·CH_2Cl_2) or attached with Krytox™ oil to a glass fiber (**5**, **6**·$CHCl_3$, **7**, **10**, **11**·0.25CH_3OH). For **4** and **9**·CH_2Cl_2 data were collected at room temperature, while for **5**, **6**·$CHCl_3$, **7**, **10** and **11**·0.25CH_3OH the crystals were cooled under a nitrogen stream at low temperature. Data were collected on Bruker SMART APEX (**4**, **9**·CH_2Cl_2) and Oxford (Type Gemini) (**5**, **6**·$CHCl_3$, **7**, **10**, **11**·0.25CH_3OH) diffractometers, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the software package SHELX-97 was used.[27] The drawings were created with the Diamond program.[28] CCDC reference numbers 821266 (**4**), 821267 (**5**), 821268 (**6**·$CHCl_3$), 821269 (**7**), 821270 (**9**·CH_2Cl_2), 821271 (**10**) and 821272 (**11**·0.25CH_3OH).

Computational details

Geometry optimizations were carried out with the ORCA 2.8, rev. 2287 software package using the BP86 functional.[29] The RI approximation was used in all the optimizations and

Table 5 Crystallographic data for compounds **10** and **11**·0.25CH_3OH

	10	**11**·0.25CH_3OH
Empirical formula	$C_{38}H_{44}N_2S_2Sb_2$	$C_{43.25}H_{45}N_2O_{5.25}S_2Sb_2W$
M	836.41	1168.32
T	110	110
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	9.1241(6)	12.2021(5)
b/Å	13.9854(9)	14.1285(5)
c/Å	14.3083(9)	14.3583(5)
α/°	90.00	82.670(3)
β/°	92.451(6)	74.980(3)
γ/°	90.00	69.615(3)
V/Å^3	1824.1(2)	2239.14(15)
Z	2	2
No. of reflections collected	7923	17 692
No. of independent reflections	3567 (R_{int} = 0.0373)	8584 (R_{int} = 0.0280)
Absorption correction	Multi-scan[26]	Multi-scan[26]
μ(Mo Kα)/mm^{-1}	1.624	3.898
R_1 [$I > 2\sigma(I)$]	0.0295	0.0233
wR_2	0.0626	0.0447
GOF on F^2	0.872	0.918

Table 4 Crystallographic data for compounds **4**, **5**, **6**·$CHCl_3$, **7** and **9**·CH_2Cl_2

	4	**5**	**6**·$CHCl_3$	**7**	**9**·CH_2Cl_2
Empirical formula	$C_{38}H_{44}BrN_2Sb$	$C_{76}H_{88}N_4SSb_2$	$C_{17}H_{17}Br_2Cl_3NSb$	$C_{19}H_{22}Br_2NSb$	$C_{33}H_{32}Cl_2N_2S_2Sb_2$
M	730.41	1333.09	623.23	545.94	835.13
T	Room temperature	110	110	110	Room temperature
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/c$	$C2/c$	$P2_1/c$	$Pbca$	$P\bar{1}$
a/Å	14.302(6)	30.5260(15)	13.5259(4)	17.248(3)	8.5344(11)
b/Å	12.633(6)	10.5847(4)	16.2912(6)	12.0752(9)	9.2918(12)
c/Å	20.722(9)	22.4533(13)	9.7040(4)	18.737(4)	11.0273(14)
α/°	90.00	90.00	90.00	90.00	98.849(2)
β/°	109.210(7)	109.267(6)	101.131(4)	90.00	102.661(2)
γ/°	90.00	90.00	90.00	90.00	96.506(2)
V/Å^3	3536(3)	6848.5(6)	2098.08(13)	3902.4(11)	833.18(19)
Z	4	4	4	8	1
No. of reflections collected	24 116	34 412	9537	11 759	8060
No. of independent reflections	6190 (R_{int} = 0.0612)	6689 (R_{int} = 0.0445)	4053 (R_{int} = 0.0299)	3813 (R_{int} = 0.0275)	2922 (R_{int} = 0.0290)
Absorption correction	Multi-scan[26]	Multi-scan[26]	Multi-scan[26]	Multi-scan[26]	Multi-scan[26]
μ(Mo Kα)/mm^{-1}	1.937	0.863	5.506	5.509	1.932
R_1 [$I > 2\sigma(I)$]	0.0559	0.0251	0.0266	0.0238	0.0262
wR_2	0.1160	0.0598	0.0622	0.0525	0.0627
GOF on F^2	1.074	0.929	0.977	0.951	1.099

relativistic effects were included using the ZORA approximation. The def2-TZVP basis set was used for the atoms Br, N, S, Sb, W, and def2-SVP for H and C, both adapted for use in conjunction with ZORA.[30] The auxiliary basis sets used were those generated by ORCA. In all geometry optimizations a Grid 4 was used for integration except for the optimizations of dimers of **7** and the *all-trans* isomer of **10** where a Grid 5 was used and the symmetry detection threshold was increased to 5.0×10^{-1}. In order to have the energy value of the *all-trans* isomer of **10** calculated at the same theory level as for the rest of the isomers, the energy was obtained from a single point calculation using the integration Grid 4. VeryTightSCF and TightOpt options were used for all the geometry optimizations and the final grid generation was suppressed. None of the optimized structures exhibited imaginary frequencies. The energy of the optimized structures obtained using the BP86 functional was evaluated using the B3LYP functional with the ORCA 2.9.1 release. In this case the RI approximation was no longer used. The basis sets used were identical to those used for the geometry optimizations. VeryTightSCF conditions and integration Grid 4 were used for all single point calculations. The energies discussed in the article are those obtained using the B3LYP functional. In order to evaluate the stabilization brought by the intramolecular coordination of the nitrogen, the energy difference between the optimized structure with the nitrogen atom coordinated to antimony and the optimized structure with the nitrogen atom uncoordinated was calculated.

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