

## Novel Rhodium–Antimony Bimetallic Complexes containing an Unusual Distibine *cis*-Eclipsed Conformation

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Rhodium–antimony bimetallic complexes, which represent rare examples of an unusual *cis*-eclipsed conformation of the phenyl groups in the ligating distibine, are synthesised and characterised by IR, mass spectrometry and X-ray crystallography.

A variety of dinuclear phosphide bridged complex and metal clusters of rhodium are known, *e.g.* [(cod)Rh( $\mu$ -PPh<sub>2</sub>)]<sub>2</sub>, [(cod)<sub>2</sub>Rh<sub>2</sub>( $\mu$ -PPh<sub>2</sub>)( $\mu$ -Cl)].<sup>1–3</sup> In contrast, until very recently only a few bi- and tri-metallic compounds with bridging R<sub>2</sub>Sb<sup>–</sup>, RSb<sup>2–</sup> organoantimony species were known,<sup>4,5</sup> but there is no report on complexation with rhodium. These types of rhodium analogues are expected to work as potential homogeneous catalysts, like their phosphido analogues. Described herein is the synthesis of Rh<sub>2</sub>(SbPh<sub>2</sub>)( $\mu$ -Cl)(cod)<sub>2</sub> **1**, and the synthesis and crystal structure of one such novel compound [Rh<sub>2</sub>(cod)<sub>2</sub>(Sb<sub>2</sub>Ph<sub>4</sub>)(SbPh<sub>2</sub>)<sub>2</sub>] **2** which contains tetra- and penta-coordinated antimony and an unusual distibine conformation.

The synthesis of **2** involves the preparation of the new monostibido-bridged dirhodium complex **1**, analogous to a monophosphido-bridged complex.<sup>2</sup> Complex **1** was synthesised

by the reaction of 1 mol of [Rh(cod)( $\mu$ -Cl)]<sub>2</sub> and 1 mol of LiSbPh<sub>2</sub> in THF. The complex is stable only at low temperatures and has been characterised by elemental analyses, IR, <sup>1</sup>H NMR and mass spectrometry.<sup>†</sup>

When the complex was treated with one more equivalent of LiSbPh<sub>2</sub> in THF the solution changed from yellow to red and tiny red crystals (78%) of **2** were slowly deposited upon solvent evaporation. The mechanism of this transformation is unknown. Complex **2** is soluble in chloroform, dichloromethane, methanol and benzene, but insoluble in hexane and diethyl ether.

After isolation and drying, elemental analyses revealed these crystals to have the empirical formula Rh(cod)(SbPh<sub>2</sub>)<sub>2</sub>. The IR spectrum of complex **1** shows a strong band at 176 cm<sup>–1</sup> which can be assigned to the Rh–Sb vibration. The mass spectrum [FAB]<sup>+</sup> of **2** shows the molecular ion peak at 1526 [M]<sup>+</sup> indicating a dimeric nature.

The X-ray structure of **2** is shown in Fig. 1.<sup>‡</sup> Complex **2** exists as a dimer and the two rhodium atoms are bridged by two distibine ligands. Each rhodium is further coordinated to an  $\eta^4$ -cod ligand. The overall geometry around the rhodium is distorted pentagonal bipyramidal. The Rh–Rh distance (4.135 Å) is much longer than the typical Rh–Rh single bond.<sup>6</sup> In the molecule, antimony atoms have two different coordination numbers. Two of the antimony atoms are tetracoordinated with distorted tetrahedral geometry while the other two atoms are pentacoordinated with distorted trigonal bipyramidal geometry. The Sb(1)–Sb(1A) bond distance 2.926(2) Å of ligating distibine is slightly longer than the Sb–Sb bond length found in distibines (2.4–2.7 Å)<sup>7</sup> but corresponds to the Sb–Sb distance found in [(Me<sub>3</sub>Si)<sub>2</sub>CHSb]<sub>4</sub><sup>8</sup> and to the ligating distibine found in (OC)<sub>5</sub>CrPh<sub>2</sub>Sb–SbPh<sub>2</sub>Cr(CO)<sub>2</sub> [2.866(1) Å].<sup>5</sup> The other Sb(2)–Sb(2A) bond length [3.155(1) Å] is longer than the normal Sb–Sb bond length but as there is a bond between Sb(2)–Sb(2A) it was concluded that there are two ligating distibines. There are also nonbonded intramolecular Sb–Sb interactions between Sb(2)–Sb(1) and Sb(2)–Sb(1A) and these intramolecular Sb–Sb distances are 3.66 and 3.78 Å, respectively. These distances are well below the sum of the van der Waal's radius of antimony (4.4 Å). In summary there are three types of Sb–Sb bonds. The average Rh–Sb distance is 2.64 Å which is comparable to that found in Rh(Cu<sub>4</sub>H<sub>38</sub>Cl<sub>2</sub>NSb<sub>2</sub>) (2.588 Å).<sup>9</sup>

It is interesting to note that the two phenyl groups of the ligating distibines Ph<sub>2</sub>Sb(1)–Sb(1A)Ph<sub>2</sub> and Ph<sub>2</sub>Sb(2)–Sb(2A)Ph<sub>2</sub> are in an unusual *cis*-eclipsed conformation rather than the usual *trans*-staggered conformation observed in distibines.<sup>5,7</sup> It is known that some ligands change their conformation during complexation but to the best of our knowledge it has not been reported for distibine ligands. The two cyclooctadiene rings with  $\eta^4$ -coordination have the same conformation.

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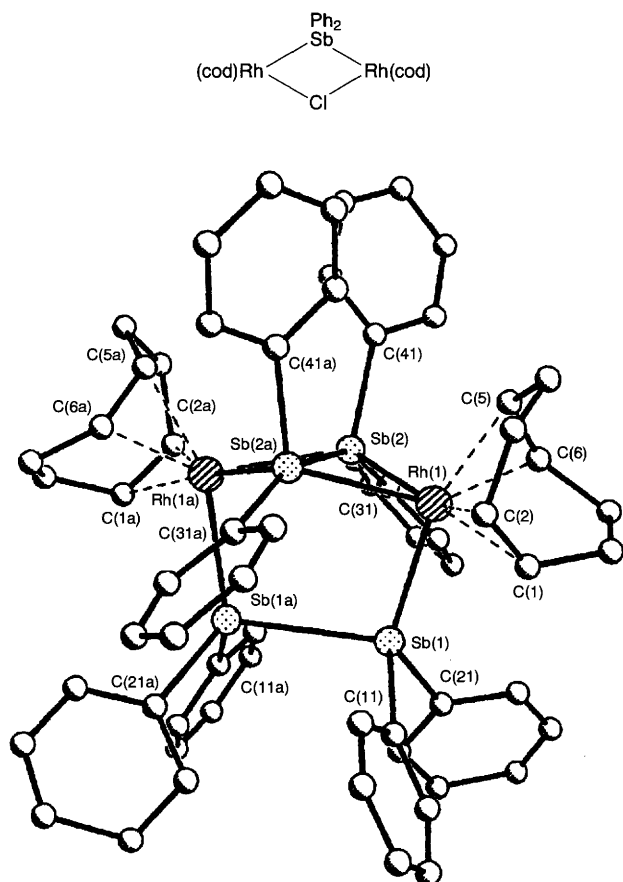


Fig. 1 Selected bond lengths (Å) and bond angles (°) for [Rh<sub>2</sub>(cod)<sub>2</sub>(Sb<sub>2</sub>Ph<sub>4</sub>)(SbPh<sub>2</sub>)<sub>2</sub>] **2**: Rh(1)–Sb(1) 2.584(1), Rh(1)–Sb(2) 2.630(1), Rh(1)–Sb(2A) 2.678(1), Sb(1)–Sb(1A) 2.926(2), Sb(2)–Rh(1A) 2.678(1), Sb(2)–Sb(2A) 3.155(1); Rh(1)–Sb(1)–C(21) 124.8(3), Rh(1)–Sb(1)–Sb(1A) 103.4(1), C(21)–Sb(1)–Sb(1A) 109.0(3), Rh(1)–Sb(2)–C(41) 111.2(3), Rh(1)–Sb(2)–Rh(1A) 102.4(1), Rh(1A)–Sb(2)–C(41) 114.3(3), C(31)–Sb(2)–Sb(2A) 156.4(3) Rh(1A)–Sb(2)–Sb(2A) 52.8(1), Rh(1)–Sb(2)–Sb(2A) 54.2(1), Sb(1)–Rh(1)–Sb(2) 89.3(1), Sb(1)–Rh(1)–Sb(2A) 91.8(1), C(11)–Sb(1)–C(21) 97.0(5), Sb(2)–Rh(1)–Sb(2A) 72.9(1)

### Footnotes

<sup>†</sup> Selected data for [Rh<sub>2</sub>(cod)<sub>2</sub>( $\mu$ -SbPh<sub>2</sub>)( $\mu$ -Cl)] **1**, yield 67%, yellow powder, mp > 114 °C (decomp.) IR spectrum exhibited bands assignable to

metal-sensitive modes of metal-phenyl and Rh-Sb vibrations.  $\nu/\text{cm}^{-1}$ : 2997, 2923, 1734, 1521, 1065, 993, 834, 485, 284, 265, 259 and 176.  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  4.39 (=CH), 1.9–2.63( $\text{CH}_2$ ), 6.67–7.12 (Ph); Mass spectrum 733  $[\text{M}]^+$ , 698  $[\text{M} - \text{Cl}]^+$ , 625  $[\text{M} - (\text{cod})]^+$ , 458  $[\text{M} - \text{SbPh}_2]^+$ , 350  $[\text{M} - (\text{cod})\text{SbPh}_2]^+$  and 275  $[\text{SbPh}_2]^+$ .

For  $[\text{Rh}_2(\text{cod})_2(\text{Sb}_2\text{Ph}_4)(\text{SbPh}_2)_2]$  **2**, red crystals, mp 143 °C. IR  $\nu/\text{cm}^{-1}$ : 3103, 2923, 1729, 1430, 1071, 870, 607, 492, 273 and 176;  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  4.46 (=CH), 2.1–2.76 ( $\text{CH}_2$ ), 6.73–7.25 (Ph); Mass spectrum  $[\text{M}]^+$  1526;  $[\text{M} - \text{SbPh}_2]^+$  1251,  $[\text{M} - \{(\text{cod})\text{SbPh}_2\}]^+$  1143,  $[\text{M} - \{\text{Rh}(\text{cod})\text{SbPh}_4\}]^+$  886,  $[\text{M} - \{\text{Rh}(\text{cod})\text{SbPh}_5\}]^+$  809,  $[\text{M} - \{\text{Rh}(\text{cod})\text{Sb}_2\text{Ph}_6\}]^+$  611,  $[\text{M} - \{\text{Rh}(\text{cod})_2\text{Sb}_2\text{Ph}_6\}]^+$  503,  $[\text{Sb}_2\text{Ph}_4]^+$  550,  $[\text{Rh}_2(\text{cod})_2]^+$  422,  $[\text{SbPH}_2]^+$  275,  $[\text{Rh}(\text{cod})]^+$  211 and  $[\text{SbPh}]^+$  198.

‡ *Crystal data* for  $\text{C}_{32}\text{H}_{32}\text{RhSb}_2$ ,  $M_r = 763.0$ , monoclinic, space group  $C2/c$ ,  $a = 19.250(3)$ ,  $b = 23.148(2)$ ,  $c = 13.927(10)$  Å,  $V = 6200.9(9)$  Å<sup>3</sup>,  $\beta = 92.33(1)^\circ$ ,  $Z = 4$ ,  $D_c = 1.635$  mg m<sup>-3</sup>, Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  nm), crystal dimensions  $0.62 \times 0.30 \times 0.15$  mm. Siemen P4/PC diffractometer yielding 4194 observed [ $F > 3\sigma(F)$ ]. The structure was solved by direct methods. The final cycle of full-matrix least-squares refinement was based on 4194 observed reflections and 317 variable parameters and converged to give final residuals  $R = 0.049$ ,  $R_w = 0.064$ . Atomic coordinates, bond lengths and angles, and thermal parameters have

been deposited at Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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