Received: 27 June 2019 | Revised: 9 October 2019 | Accepted: 5 November 2019
DOI: 10.1002/aoc.5393

FULL PAPER

Applied Organometallic Chemistry WILEY

Hypercoordinated diorganoantimony(III) compounds of types $[2\text{-}(Me_2NCH_2)C_6H_4]_2SbL$ and $[PhCH_2N(CH_2C_6H_4)_2]SbL$ ($L = Cl, ONO_2, OSO_2CF_3$). Synthesis, structure and catalytic behaviour in the Henry reaction

Răzvan Şuteu[1] | **Ciprian I. Raţ**[1] | **Cristian Silvestru**[1] | **Andrada Simion**[2] | **Natalia Candu**[2] | **Vasile I. Pârvulescu**[2] | **Anca Silvestru**[1]

[1]Department of Chemistry, Supramolecular Organic and Organometallic Chemistry Centre (SOOMCC), Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai University, 11 Arany Janos, 400028 Cluj-Napoca, Romania

[2]Department of Organic Chemistry, Biochemistry and Catalysis, Faculty of Chemistry, University of Bucharest, 4-12 Regina Elisabeta Av. S3, 030018 Bucharest, Romania

Correspondence
V. I. Pârvulescu, Department of Organic Chemistry, Biochemistry and Catalysis, Faculty of Chemistry, University of Bucharest, 4-12 Regina Elisabeta Av. S3, 030018 Bucharest, Romania.
Email: vasile.parvulescu@chimie.unibuc.ro

A. Silvestru, Department of Chemistry, Supramolecular Organic and Organometallic Chemistry Centre (SOOMCC), Faculty of Chemistry and Chemical Engineering, Babe-Bolyai University, 11 Arany Janos, 400028 Cluj-Napoca, Romania.
Email: ancas@chem.ubbcluj.ro

Funding information
National University Research Council of Romania, CNCS-UEFISCDI, Grant/Award Number: PN-III-P4-ID-PCE-2016-0857

The compounds $[2\text{-}(Me_2NCH_2)C_6H_4]_2SbL$ ($L = ONO_2$ (**2**), OSO_2CF_3 (**3**)) and $[PhCH_2N(CH_2C_6H_4)_2]SbL$ ($L = ONO_2$ (**5**), OSO_2CF_3 (**6**)) were prepared by reacting $[2\text{-}(Me_2NCH_2)C_6H_4]_2SbCl$ (**1**) and $[PhCH_2N(CH_2C_6H_4)_2]SbCl$ (**4**), respectively, with the appropriate silver(I) salt in a 1:1 molar ratio. The new species **2–6** were structurally characterized in solution using multinuclear NMR and in the solid state using infrared spectroscopy. The solid-state structures for compounds **2**, **4** and **6,** as well as for the hydrolysis ionic product $[\{2\text{-}(Me_2N^+HCH_2)C_6H_4\}\{2\text{-}(Me_2NCH_2)C_6H_4\}SbOH][CF_3SO_3]^-$ (**3h**) were determined using single-crystal X-ray diffraction. Medium to strong intramolecular N→ Sb interactions were observed in all these four compounds, thus resulting in hypercoordinated organoantimony(III) species *14-Sb-6* in **2** and *10-Sb-4* in the cation of **3h** and in **4** and **6**. Compounds **1–6** and the starting amines $PhCH_2NMe_2$ and $PhCH_2N(CH_2C_6H_4Br\text{-}2)_2$ were investigated as catalysts in the Henry (nitroaldol) addition of nitromethane to benzaldehyde. The activity of compounds **1–6** resulted as an effect of the cooperation of the positively charged antimony with the negatively charged nitrogen.

KEYWORDS
catalytic activity, diorganoantimony(III) complexes, Henry (nitroaldol) reaction, hypercoordination, structural investigation

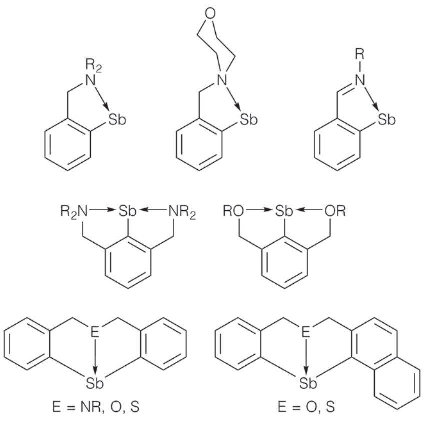
1 | INTRODUCTION

Organoantimony(III) compounds bearing organic groups capable of forming chelate rings by intramolecular E→Sb (E = N, O, S) interactions have attracted increased interest during the last few decades due to the related structural aspects and the increased stability of unusual species, but also due to their biological and catalytic activity.[1] The intramolecular E→Sb coordination usually results in E→ Sb–X *3c-4e* linear systems, designated as hypercoordinated (hypervalent) *N–M–L* species.[2] Organic groups with one or two pendant arms, capable of (*C*,*E*)-, (*E*,*C*,*E*)- or (*C*,*E*,*C*)-coordination behaviour (E = N, O, S) (Scheme 1), e.g. $2\text{-}(R_2NCH_2)C_6H_4$ (R = Me,[3] Et,[4] ^{i}Pr[4,5]), $2\text{-}[Me_2NCH(Me)]C_6H_4$,[3f, j] $2\text{-}[O(CH_2CH_2)_2NCH_2]C_6H_4$,[6] $2\text{-}(RN{=}CH)C_6H_4$ (R = $2',4',6'\text{-}Me_3C_6H_2$, $2',6'\text{-}{}^{i}Pr_2C_6H_3$)[3t, 7] or related ones,[8] and $2,6\text{-}(Me_2NCH_2)_2C_6H_3$,[9] $2,6\text{-}[MeN(CH_2CH_2)_2NCH_2]_2C_6H_3$,[10] $2,6\text{-}(ROCH_2)_2C_6H_3$ (R = Me,[9e, 11] ^{t}Bu,[9e, 11a, d, 12] Mes[11d]), $2\text{-}(Me_2NCH_2)\text{-}6\text{-}(ROCH_2)C_6H_3$ (R = Me,[13] ^{t}Bu[12c]) as well as $RN(CH_2C_6H_4)_2$ (R = Me,[14] Et,[14b] ^{i}Pr,[14b] ^{i}Bu,[14b] ^{t}Bu,[14b, 15] Cy,[14b, 15c, 16] Ph[14b, 15c, 17]), $O(CH_2C_6H_4)_2$[14b, 18] and $E(CH_2C_6H_4)(CH_2C_6H_{10})$ (E = O, S),[19] were already employed as ligands in organoantimony(III) species and some of these compounds were found to exhibit relevant applications in organic synthesis.

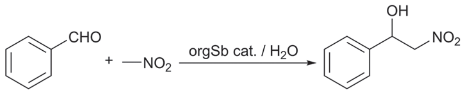
The soft nucleophilic character of the air-stable 1,5-azastibocines, which display strong transannular N→Sb interactions, recommend them as efficient transmetallating reagents, more friendly than the hard and moisture-sensitive organolithium, organomagnesium or organozinc derivatives. Compounds of type $[RN(CH_2C_6H_4)_2]SbC{\equiv}CR'$ (R = Me, ^{i}Pr, ^{t}Bu; R′ = Ph, $4\text{-}MeC_6H_4$, $4\text{-}FC_6H_4$) were used in the catalytic synthesis of alkynyl ketones or diarylacetylenes by cross-coupling reactions and an increased reactivity of these azastibocine species was noticed compared to the related (arylethynyl) diphenylantimony(III) derivatives $Ph_2SbC{\equiv}CR'$. An increased efficiency was observed, as well, when more electron-donating and bulkier substituents (^{i}Pr, ^{t}Bu) at nitrogen were used.[14] Similar compounds based on a butterfly-like skeleton, $[{}^{t}BuN(CH_2C_6H_4)_2]SbR$ (R = aryl), proved to be good aryl donors in Rh-catalysed 1,4-conjugate addition to α,β-unsaturated carbonyl derivatives[15b] and 1,2-addition to functionalized aldehydes.[15c] In contrast, palladium catalysts favoured the competing Heck arylation of methyl vinyl ketone by azastibocine derivatives.[15b] 1,5-Azastibocines of the type $[RN(CH_2C_6H_4)_2]SbOSO_2CF_3$ were reported to be efficient catalysts in the direct Mannich reaction in water under mild conditions,[16a] and in the allylation of aldehydes with tetraallyltin.[17]

The dinuclear oxide $[2,6\text{-}(Me_2NCH_2)_2C_6H_3SbO]_2$ absorbs reversibly CO_2,[9f] while the $[2,6\text{-}(Me_2NCH_2)_2C_6H_3SbS]_2$ analogue exhibits a similar behaviour towards CS_2.[9i]

The Henry reaction is largely used in organic chemistry as a means of C—C bond formation by the coupling of a nucleophile generated from a nitroalkane with a carbonyl electrophile in base catalysis, thus resulting in β-nitroalcohols which are valuable intermediates in organic synthesis. Since 1895 when the reaction was reported by Louis Henry,[20] various organic or inorganic catalysts have been employed in asymmetric Henry reactions, e.g. triethylamine, LDA, TMEDA, alkali metal hydroxides, alkoxides or carbonates, barium hydroxide, tetrabutylammonium hydroxide or transition metal complexes.[21] Efforts are continuously made to find active species with high selectivity, air- and moisture-stable compounds with low toxicity that are of low cost and readily available. During the last few years our research interest has been focused on hypercoordinated organoantimony(III) compounds with N→Sb intramolecular interactions.[3h, i, k-n, s-w, 4–7] So far, no organoantimony compound has been employed as catalyst in Henry reactions. Here we report several new hypercoordinated diorganoantimony(III) compounds, namely $[2\text{-}(Me_2NCH_2)C_6H_4]_2SbL$ (L = ONO_2 (**2**), OSO_2CF_3 (**3**)) and $[PhCH_2N(CH_2C_6H_4)_2]SbL$ (L = Cl (**4**), ONO_2 (**5**), OSO_2CF_3 (**6**)), which, based on their stability and their dual Lewis acid/base properties, might act as catalysts in the Henry (nitroaldol) reaction. Thus, we decided to investigate the influence of the structure and the electronic environment in compounds **2–6** upon the catalytic efficiency in a Henry reaction (Scheme 2).



SCHEME 1 Examples of organoantimony moieties containing (*C*,*E*)-, (*E*,*C*,*E*)- or (*C*,*E*,*C*)-ligands



SCHEME 2 Henry reaction catalysed by hypercoordinated diorganoantimony(III) compounds

2 | EXPERIMENTAL

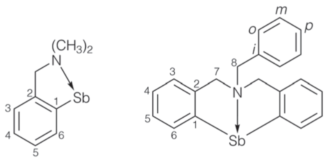
2.1 | Materials and procedures

Experiments involving air-sensitive compounds were performed under argon atmosphere using Schlenk techniques. Organic solvents were dried and freshly distilled under argon prior to use. Starting materials such as ^{n}BuLi, $AgNO_3$ and AgOTf were commercially available and were used as received, or were prepared according to literature procedures: $[2\text{-}(Me_2NCH_2)C_6H_4]_2SbCl$ (**1**),[3c, h] $PhCH_2N(CH_2C_6H_4Br\text{-}2)_2$.[22] ^{1}H NMR, ^{13}C{H} NMR and ^{19}F{H} NMR spectra were recorded in $CDCl_3$, at room temperature, with a Bruker Avance III 400 instrument. The ^{1}H and ^{13}C chemical shifts are reported in δ units (ppm) relative to tetramethylsilane, considering the residual peak of the solvent (^{1}H, 7.26 ppm; ^{13}C, 77.16 ppm). The ^{1}H and ^{13}C resonances were assigned using 2D NMR experiments (COSY, HSQC, HMBC) according to the numbering schemes shown in Scheme 3. For the ^{19}F NMR spectra, the chemical shifts are reported in ppm relative to $CFCl_3$. The NMR spectra were processed using the MestReNova software.[23] Infrared (IR) spectra were recorded with a BioRad FTS-165 machine as KBr pellets. ESI+ mass spectra were recorded using a Thermo Scientific Orbitrap XL spectrometer equipped with a standard ESI/APCI source. Elemental analyses were performed with a Flash EA 1112 analyser. Melting points were measured with an Electrothermal 9200 apparatus and are not corrected.

2.2 | Syntheses

2.2.1 | Synthesis of $[2\text{-}(Me_2NCH_2)C_6H_4]_2SbONO_2$ (2)

A mixture of **1** (0.686 g, 1.612 mmol) and $AgNO_3$ (0.274 g, 1.612 mmol) in acetone (20 ml) was stirred for 3 h at room temperature, in the absence of light. After the removal of the solvent, the compound was extracted in CH_2Cl_2. Evaporation of the solvent at reduced pressure resulted in compound **2** as a beige solid. Yield: 0.520 g (71%), m.p. 154°C. Anal. found: C 47.68, H 5.12, N 9.47%; calcd for $C_{18}H_{24}N_3O_3Sb$ (MW 452.17): C 47.81, H 5.35, N 9.29%. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 2.33$ (s, br, 12H, NCH_3), 3.74 (s, br, 4H, CH_2N), 7.24–7.39 (m, 6H, H-3,H-4,H-5), 7.62 (s, br, 2H, H-6). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): $\delta = 45.76$ (s, NCH_3), 66.32 (s, CH_2N), 128.21 (s, br, C-5), 128.72 (s, C-3), 129.64 (s, br, C-4), 136.10 (s, br, C-6), 143.85 (s, br, C-2), 146.56 (s, br, C-1).



SCHEME 3 Numbering schemes for NMR resonance assignments

2.2.2 | Synthesis of $[2\text{-}(Me_2NCH_2)C_6H_4]_2SbOSO_2CF_3$ (3)

Compound **3** was prepared from **1** (1.049 g, 2.473 mmol) and $AgOSO_2CF_3$ (0.632 g, 2.473 mmol) using a similar procedure to that for compound **2**. Compound **3** was obtained as a beige solid. Yield: 0.933 g (70%), m. p. 168°C. Anal. found: C 42.11, H 4.37, N 5.01%; calcd for $C_{19}H_{24}F_3N_2O_3SSb$ (MW 539.23): C 42.32, H 4.49, N 5.20%. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 2.57$ (s, br, 12H, NCH_3), 3.81 (s, br, 4H, CH_2N), 7.27–7.49 (m, 6H, H-3,H-4,H-5), 7.83 (s, br, 2H, H-6). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): $\delta = 45.38$ (s, NCH_3), 65.41 (s, CH_2N), 120.78 (q, CF_3, $^{1}J_{FC} = 321$ Hz), 129.02 (s, br, C-5), 130.36 (s, br, C-3 and C-4), 135.69 (s, br, C-6), 145.04 (s, br, C-1 and C-2). ^{19}F{^{1}H} NMR ($CDCl_3$, 376.5 MHz): $\delta = -78.06$ (s, CF_3).

2.2.3 | Synthesis of $[PhCH_2N(CH_2C_6H_4)_2]SbCl$ (4)

A solution of ^{n}BuLi in hexane (1.188 g, 7.4 ml, 2.5 M, 18 mmol) was added dropwise to a solution of $PhCH_2N(CH_2C_6H_4Br\text{-}2)_2$ (4.13 g, 9 mmol) in diethyl ether (70 ml), at −30°C, and the reaction mixture was left under stirring for 2 h at this temperature. Then the temperature was decreased to −78°C, solid $SbCl_3$ (2.116 g, 9 mmol) was added and the reaction mixture was stirred overnight. The solvent was removed in vacuum and the product was extracted from the remaining colourless solid with CH_2Cl_2. The organic phase was washed with water (3 × 20 ml) and dried over anhydrous $MgSO_4$. After filtration, removal of solvent under reduced pressure and washing with *n*-hexane, compound **4** was isolated as a beige solid. Yield: 2.87 g (70%), m.p. 173–174°C. Anal. found: C 56.72, H 4.47, N 3.02%; calcd for $C_{21}H_{19}ClNSb$ (MW 442.60): C 56.99, H 4.33, N 3.16%. ^{1}H NMR ($CDCl_3$, 400 MHz): AB spin system with A at $\delta = 3.89$ and B at $\delta = 4.12$ (4H, $^{2}J_{H,H} = 14.6$ Hz, CH_2, H-7), $\delta = 4.06$ (s, 2H, CH_2, H-8), 7.11 (d, 2H, $^{3}J_{H,H} = 7.4$ Hz, H-3), 7.27–7.34 (m, 2H, H-4 + 2H, C_6H_5-*ortho*), 7.38–7.47 (m, 2H, H-5 + 3H, C_6H_5-*meta* and -*para*), 8.29 (d, 2H, $^{3}J_{H,H} = 7.6$ Hz, H-6). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): $\delta = 57.73$ (s, C-8), 57.79 (s, C-7), 125.68 (s, C-3), 128.98 (s,

C_6H_5-*meta*), 129.16 (s, C_6H_5-*para*), 129.23 (s, C-4), 129.35 (s, C-5), 131.39 (s, C_6H_5-*ortho*), 132.24 (s, C_6H_5-*ipso*), 135.86 (s, C-6), 140.25 (s, C-1), 142.60 (s, C-2).

2.2.4 | Synthesis of $[PhCH_2N(CH_2C_6H_4)_2]SbONO_2$ (5)

Compound **5** was prepared from **4** (0.268 g, 0.600 mmol) and $AgNO_3$ (0.102 g, 0.600 mmol) using a similar procedure to that for compound **2**. Compound **5** was obtained as a beige solid. Yield: 0.274 g (96%), m.p. 175°C. Anal. found: C 53.51, H 3.87, N 5.77%; calcd for $C_{21}H_{19}N_2O_3Sb$ (MW 469.15): C 53.76, H 4.08, N 5.97%. ^1H NMR ($CDCl_3$, 400 MHz): AB spin system with A at $\delta = 3.97$ and B at $\delta = 4.24$ (4H, $^2J_{H,H} = 14.5$ Hz, CH_2, H-7), $\delta = 4.16$ (s, 2H, CH_2, H-8), 7.17 (d, 2H, $^3J_{H,H} = 7.2$ Hz, H-3), 7.29–7.37 (m, 2H, H-4 + 2H, C_6H_5-*ortho*), 7.40 (t, 2H, $^3J_{H,H} = 7.4$ Hz, H-5), 7.44–7.49 (m, 3H, C_6H_5-*meta* and -*para*), 7.88 (d, 2H, $^3J_{H,H} = 7.5$ Hz, H-6). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): $\delta = 58.39$ (s, C-8), 58.71 (s, C-7), 125.98 (s, C-3), 129.18 (s, C_6H_5-*meta*), 129.57 (s, C_6H_5-*para*), 129.70 (s, C-4), 129.77 (s, C-5), 131.45 (s, C_6H_5-*ipso*), 131.55 (s, C_6H_5-*ortho*), 135.45 (s, C-6), 140.15 (s, C-1), 142.65 (s, C-2).

2.2.5 | Synthesis of $[PhCH_2N(CH_2C_6H_4)_2]SbOSO_2CF_3$ (6)

Compound **6** was prepared from **4** (0.210 g, 0.474 mmol) and $AgOSO_2CF_3$ (0.122 g, 0.474 mmol) using a similar procedure to that for compound **3**. Compound **6** was obtained as a beige solid. Yield: 0.264 g (78%), m.p. 175°C. Anal. found: C 47.28, H 3.47, N 2.27%; calcd for $C_{22}H_{19}F_3NO_3SSb$ (MW 556.21): C 47.51, H 3.44, N 2.52%. ^1H NMR ($CDCl_3$, 400 MHz): AB spin system with A at $\delta = 4.06$ and B at $\delta = 4.33$ (4H, $^2J_{H,H} = 14.5$ Hz, CH_2, H-7), $\delta = 4.20$ (s, 2H, CH_2, H-8), 7.20 (d, 2H, $^3J_{H,H} = 7.2$ Hz, H-3), 7.30–7.39 (m, 2H, H-4 + 2H, C_6H_5-*ortho*), 7.41–7.53 (m, 2H, H-5 + 3H, C_6H_5-*meta* and -*para*), 8.02 (d, 2H, $^3J_{H,H} = 7.2$ Hz, H-6). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): $\delta = 59.54$ (s, C-8), 60.21 (s, C-7), 125.58 (s, C-3), 129.39 (s, C_6H_5-*meta*), 130.03 (s, C-5 and C_6H_5-*para*), 130.20 (s, C-4), 130.76 (s, C_6H_5-*ipso*), 131.61 (s, C_6H_5-*ortho*), 135.66 (s, C-6), 140.83 (s, C-1), 142.55 (s, C-2). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 376.5 MHz): $\delta = -77.36$ (s, CF_3).

2.3 | Crystal structure determination

Single crystals suitable for X-ray diffraction studies were grown from a mixture of CH_2Cl_2 and *n*-hexane (1/4, v/v). The details of the crystal structure determination and refinement for compounds **2**, **3h**, **4** and **6** are given in Table S1 (supporting information). The crystals were mounted on MiTeGen microMounts cryoloops and data were collected with a Bruker SMART APEX (for **2**, **4** and **6**, at 294 K) and with a Bruker D8 VENTURE (for **3h**, at 100 K), using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were refined with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atom H1 in **3h** was located in a difference Fourier map and freely refined. All the other hydrogen atoms were placed in fixed, idealized positions and refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement, the software packages SHELX-2014/7, included in WinGX[24,25] (for **2**, **4** and **6**), and Bruker APEX3 (for **3h**)[24] were used. Intermolecular interactions were identified with PLATON.[26] Visualizations were created with the Diamond program.[27]

2.4 | Catalysis

All reagents were purchased from Sigma-Aldrich and used as received without further purification. Benzaldehyde (0.5 mmol), nitromethane (10 mmol) and the corresponding catalyst were added to a glass sealed vial containing 3 ml of ultrapure water. The reaction mixture was left under stirring at 1200 rpm for 24 h at 50°C, and then filtered, concentrated and silylated (50 μl of pyridine, 100 μl of *N*,*O*-bis(trimethylsilyl)trifluoroacetamide and trimethylchlorosilane). The water-soluble catalysts were firstly precipitated using NaI and then separated by filtration. The recovered products were analysed using a GC-MS (Thermo Electron Corporation) instrument, Trace GC Ultra and DSQ, Trace GOLD: TG-5SilMS column with the following characteristics: 30 mm × 0.25 mm × 0.25 mm, working with a temperature programme (50°C (2 min) to 250°C at 10°C min^{-1} (hold 10.00 min) for a total run time of 32 min) at a pressure of 0.38 Torr with He as the carrier gas. NMR analysis of the products was carried out using a Bruker Avance III UltraShield 500 MHz spectrometer, operating at 500 MHz for ^1H NMR and 125.8 MHz for ^{13}C NMR. The NMR analysis of 2-nitro-1-phenylethanol corresponded to: ^1H NMR ($CDCl_3$, 500.13 MHz): $\delta = 3.88$ (s, br, 1H, O*H*), 4.50–4.63 (m, 2H, CH_2NO_2), 5.47 (m, 1H, C*H*OH), 7.41–7.57 (m, 5H, C_6H_5); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.77 MHz): $\delta = 70.99$ (s, *C*HOH), 81.22 (s, CH_2NO_2), 125.93 (s, C_6H_5), 129.05 (s, C_6H_5), 129.14 (s, C_6H_5), 138.08 (s, C_6H_5).

2.5 | Theoretical calculations

Theoretical calculations for **1–6** were performed with Gaussian 09, Revision E.01,[28] using the B3LYP functional[29] and the def2-TZVP basis set.[30] The dispersion corrections were accounted for using the D3 version of Grimme's dispersion with Becke–Johnson damping.[31] The Cartesian coordinates of the calculated molecular structures of **1–6** are given in Tables S3–S8 (supporting information).

3 | RESULTS AND DISCUSSION

3.1 | Synthesis

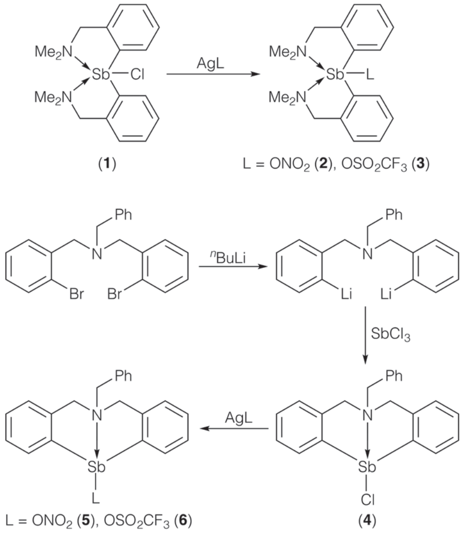
Diorganoantimony(III) compounds of the general formulae $[2\text{-}(Me_2NCH_2)C_6H_4]_2SbL$ and $[PhCH_2N(CH_2C_6H_4)_2]SbL$ (L = ONO_2, OSO_2CF_3) were prepared by ligand exchange reactions between the corresponding diorganoantimony(III) chlorides **1** and **4**, respectively, and the appropriate silver salt in a 1:1 molar ratio, as depicted in Scheme 4. Compounds **2–6** are microcrystalline solids, soluble in common organic solvents.

3.2 | Spectroscopic characterization

The ^1H NMR, $^{13}C\{H\}$ NMR and $^{19}F\{H\}$ NMR spectra confirmed the formation of the desired compounds and are consistent with the presence of only one species in solution. In **3** and **4** the methylene and the methyl protons in the CH_2NMe_2 moiety give broad singlet resonances at room temperature, thus suggesting a fast dynamic process in solution.[3h, 32] The non-equivalent CH_2NCH_2 protons in the fused diheterocyclic skeleton of **4–6** appear as an AB spin system in the ^1H NMR spectra, while the CH_2 protons in the $PhCH_2N$ moiety give a sharp singlet resonance, similar to the situation found for the diorganobismuth(III) analogues.[33]

Compounds **2** and **5** show in their IR spectra strong, broad bands at 1458/1285 cm^{-1} and 1495/1270 cm^{-1}, respectively, which might suggest a chelating bidentate coordination of the anionic NO_3^- ligand.[34] The IR spectra of **3** and **6** show strong bands at 1292/1030 cm^{-1} and 1265/1030 cm^{-1}, respectively, which were assigned to the $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$ vibrations of the triflate anion.[35]

The ESI+ mass spectra show in all cases the base peak at m/z experimental values of 389.0962 (**2**), 389.0965 (**3**), 406.0537 (**4** and **5**) and 406.0554 (**6**), corresponding to the cations $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_2Sb^+]$ (calcd m/z value 389.0972) and $[\{PhCH_2N(CH_2C_6H_4)_2\}Sb^+]$ (calcd m/z value 406.0550), respectively.



SCHEME 4 Preparation of compounds **2–6**

3.3 | Solid-state structures

The molecular structures for **2**, **3h**, **4** and **6** were established using single-crystal X-ray diffraction and are depicted in Figures 1–4. Selected interatomic distances and bond angles are summarized in Table 1. For **4**, the unit cell contains two independent molecules with very

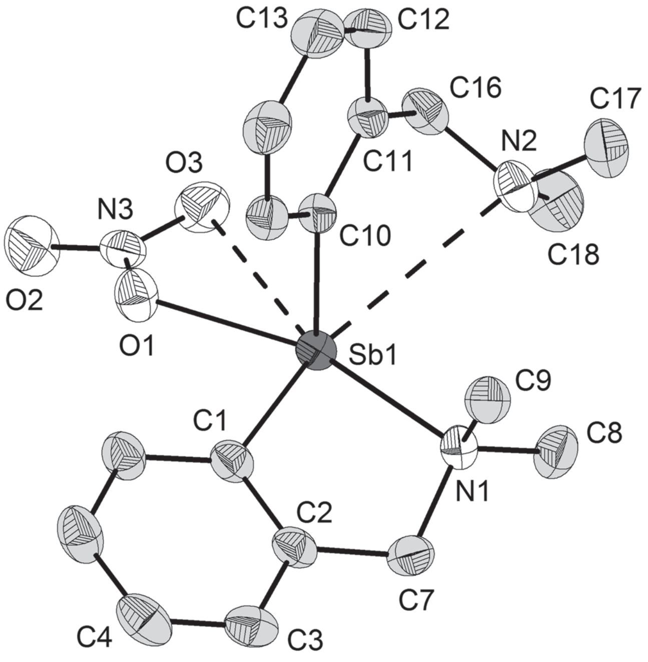


FIGURE 1 Molecular structure of isomer $(C_{Sb1})(pS_{N1},pR_{N2})$-**2**. Thermal ellipsoids are drawn at 30% probability (hydrogen atoms are omitted for clarity)

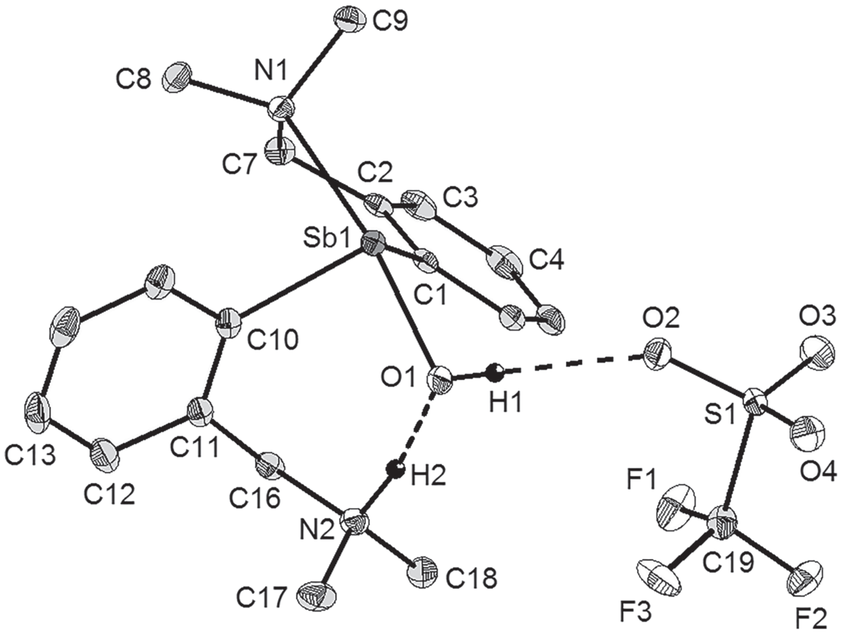


FIGURE 2 Structure of isomer (C_{Sb1}) (pS_{N})-**3h**. Thermal ellipsoids are drawn at 40% probability (hydrogen atoms, except H(1) and H(2), are omitted for clarity)

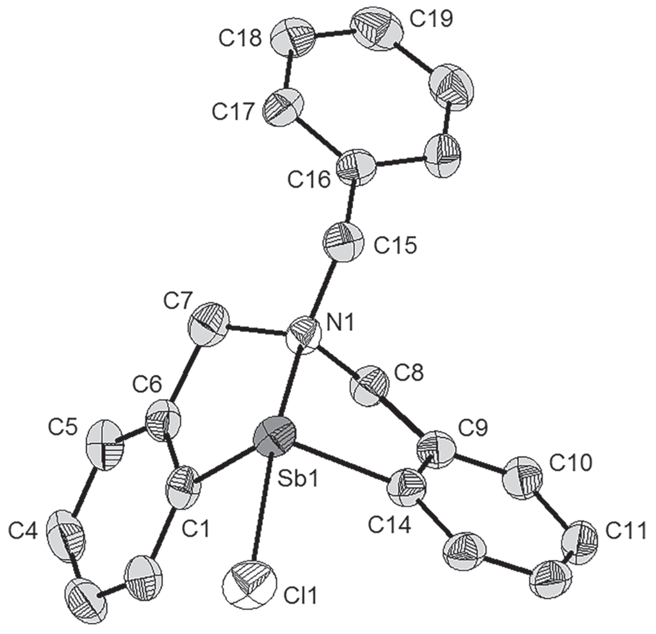


FIGURE 3 Molecular structure of isomer $(pS_{\mathrm{N1}},pS_{\mathrm{N2}})$-**4a**. Thermal ellipsoids are drawn at 30% probability (hydrogen atoms are omitted for clarity)

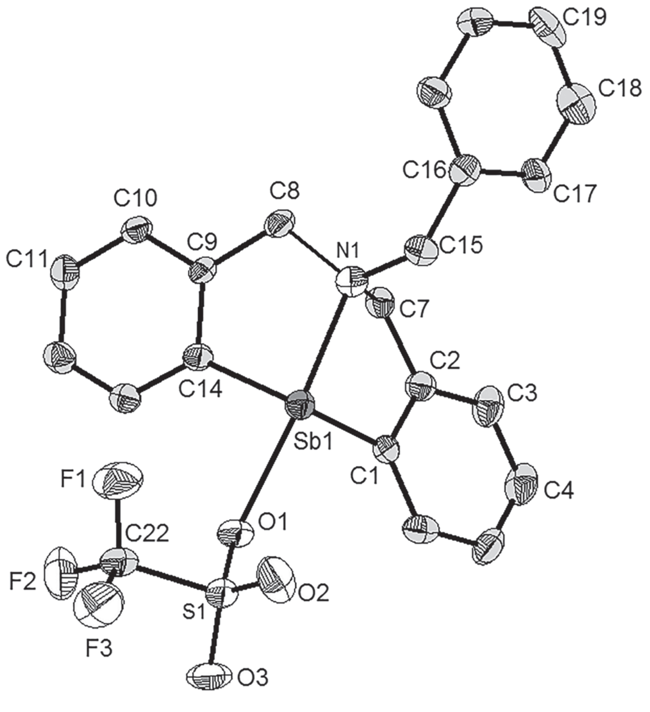


FIGURE 4 Molecular structure of **6**. Thermal ellipsoids are drawn at 30% probability (hydrogen atoms are omitted for clarity)

similar molecular parameters; therefore only data for molecule **4a** are listed in Table 1 and included in the subsequent discussion (molecule **4b** is shown in Figure S7 and its molecular parameters are listed in Table S2 in the supporting information).

In **2**, the nitrogen atoms of both 2-$(Me_2NCH_2)C_6H_4$ substituents on the antimony atom are intramolecularly coordinated to the metal (Figure 1). The two N→Sb interactions are significantly different (N(1)→Sb(1) 2.393(3)/N(2)→Sb(1) 3.219 Å, cf. Σr_{vdW} (Sb,N) 3.74 Å[36], similar to the situation found in $[2\text{-}(Me_2NCH_2)C_6H_4]_2SbX$ (X = Cl, Br, I),[3c,h] the stronger one being *trans* to the O(1) atom, while the weaker one is established *trans* to the C(1) atom. The intramolecular N→Sb interactions result in the formation of two five-membered NC_3Sb chelate rings which are not planar, but folded along the imaginary Sb···$C_{methylene}$ axis, with the nitrogen atom placed out of the best plane defined by the residual SbC_3 fragment. This induces planar chirality (with the aromatic ring and the nitrogen atom as chiral plane and pilot atom, respectively; isomers are given as S_N and R_N).[37] The NO_3^- anionic ligand acts as an anisobidentate (chelating) ligand (O(1)–Sb(1) 2.375(3)/O(3)→Sb(1) 3.145(3) Å, cf. Σr_{vdW} (Sb,O) 3.60 Å[36]), with the weaker O(3)→Sb(1) interaction bisecting the open N(2)···Sb(1)–O(1) bond angle (120.20(9)°). This results in a *14-Sb-6* hypercoordinated species for which the overall coordination geometry can be described as distorted pentagonal pyramidal, with the C10 atom in the apical position. Due to intramolecular N→Sb and O→Sb interactions, the metal centre becomes chiral (*chelate-induced Sb chirality*[1b,3n,v]), a behaviour which can be described in terms of C_{Sb} and A_{Sb} isomers.[38] Therefore the crystal of **2** contains a 1:1 mixture of $(C_{Sb1})(pS_{N1},pR_{N2})$-**2** and $(A_{Sb1})(pR_{N1},pS_{N2})$-**2** isomers.

Our attempts to grow single crystals of **3** resulted in a hydrolysis product, namely the ionic species $[\{2\text{-}(Me_2N^+HCH_2)C_6H_4\}\{2\text{-}(Me_2NCH_2)C_6H_4\}SbOH][CF_3SO_3]^-$ (**3h**), probably through the formation of ionic species $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_2Sb(H_2O)]^+[CF_3SO_3]^-$ and, subsequently, abstraction of one of the hydrogen atoms in the water molecule by the nitrogen of the weakly coordinated pendant arm. This fact is also supported by density functional theory calculations. In **3h**, the remaining N(1)→Sb(1) intramolecular interaction is a strong one (2.545 Å), while the Sb–O bond length is just at the border of the sum of the covalent radii of the two elements (Sb(1)–O(1) 2.079(1) Å, cf. Σr_{cov} (Sb,O) 2.07 Å[36]). In this way a distorted pseudo-trigonal bipyramidal ("see-saw") coordination geometry is achieved around antimony in the hypercoordinated *10-Sb-4* cation, with the intramolecularly coordinated nitrogen and the hydroxo oxygen in apices (N(1)–Sb(1)–O(1) 159.65(4)°). The crystal of **3h** contains a 1:1 mixture of $(C_{Sb1})(pS_{N1})$-**3h** and $(A_{Sb1})(pR_{N1})$-**3h** isomer cations. It should also be noted that, in addition to a strong intramolecular hydrogen bond which involves the protonated nitrogen and the oxygen bonded to the metal centre (N(2)···O(1) 2.591(2) Å, H(2)···O(1) 1.60 Å, N(2)–H(2)···O(1) 168.00°), another strong cation–anion hydrogen bond is also established between the hydroxo group and an oxygen of the triflate anion (O(1)···O(2) 2.871(2) Å, H(1)···O(2) 2.14(2) Å, O(1)–H(1)···O(2) 176.7(16)°) (Figure 2).

The molecular structures of **4** (Figure 3) and **6** (Figure 4) show several similarities, with respect to the diorganoantimony(III) fragment. The nitrogen atom is involved in a strong transannular N→Sb intramolecular interaction (Table 1) of a magnitude similar to that previously observed in the related species $[RN(CH_2C_6H_4)_2]SbL$ (L = Cl, R = ^tBu,[15d] Cy[16b]; L = OSO_2CF_3, R = Cy,[16a] Ph[17]). This results in a butterfly-like structure, containing two fused NC_3Sb five-membered rings and, as a consequence, to a *10-Sb-4* hypercoordinated species with a distorted pseudo-trigonal bipyramidal ("see-saw") environment about antimony (Cl(1)–Sb(1)–N(1) 160.31(10)° in **4a**; O(1)–Sb(1)–N(1) 153.5(2)° in **6**). If the weaker Sb(1)···O(2) contact (3.473(6) Å, cf. Σr_{vdW} (Sb,O) 3.60 Å[36]) is also considered, **6** might be alternatively described as a *12-Sb-5* hypercoordinated species. The chirality induced by the nonplanar NC_3Sb five-membered rings results in 1:1 racemic mixtures of (pR^1,pR^2) and (pS^1,pS^2) isomers (superscript indices "1" and "2" are assigned for the two fused NC_3Sb rings in a butterfly-like molecule) in the crystals of **4** (for both **4a** and **4b** molecules) and **6**, respectively.

A closer look to the solid-state structures of these compounds reveals interesting supramolecular architectures. Thus, pairs of $(C_{Sb1})(pS_{N1},pR_{N2})$-**2** and $(A_{Sb1})(pR_{N1},pS_{N2})$-**2** isomers are connected through intermolecular Sb···π ($Ar_{centroid}$) interactions (Sb(1)···$Ar_{centroid}$\{C(1′)–C(6′)\} 3.94 Å) and the resulting dimer associations are further supported by C–H···O interactions (C(7)–H(7B)$_{methylene}$···O(1′) 2.57 Å, cf. Σr_{vdW}(O,H) 2.60 Å[36]) (Figure S1 in the supporting information). Such dimeric units are associated into a honeycomb-type layer in which a central dimer unit is connected to six other dimers through both C–H···π ($Ar_{centroid}$) interactions (C(18)–H(18C)$_{methyl}$···$Ar_{centroid}$\{C(1′a)–C(6′a)\} 3.06 Å, γ = 15.6°) (i.e. H···$Ar_{centroid}$ contacts shorter than 3.1 Å, and an angle γ between the normal to the aromatic ring and the line defined by the H atom and $Ar_{centroid}$ smaller than 30°)[39] and C–H···O interactions (C(14)–H(14)$_{aryl}$···O(3′b) 2.51 Å), with no further contacts between parallel layers (for details, see Figures S2 and S3 in the supporting information).

In the crystal of **3h**, chains of same type cation isomers, i.e. $(C_{Sb1})(pS_{N1})$-**3h** and $(A_{Sb1})(pR_{N1})$-**3h**, respectively, and triflate anions are formed along the *a*-axis based on C–H···π ($Ar_{centroid}$) (C(7)–H(7B)$_{methylene}$···$Ar_{centroid}$\{C(1c)–C(6c)\} 2.87 Å, γ = 23°) and C–H···O contacts (C(9)–H(9C)$_{methyl}$···O(3c) 2.56 Å; C(17a)–H(17Aa)$_{methyl}$···O(4) 2.55 Å) (Figure S4 in the supporting information). Such parallel chains alternate and are connected into a supramolecular three-dimensional architecture through further C–H···O contacts (C(8)–H(8B)$_{methyl}$···O(3d) 2.45 Å; C(17)–H(17C)$_{methyl}$···O(4e) 2.48 Å) (for details, see Figures S5 and S6 in the supporting information).

In the crystal of **4**, pairs of isomers of the same type from the two independent molecules are associated in

TABLE 1 Selected interatomic distances (Å) and bond angles (°) for compounds **2**, **3h**, **4**(molecule 4a) and **6**

2		**3h**		**4a**		**6**	
Sb(1)–C(1)	2.163(4)	Sb(1)–C(1)	2.1615(16)	Sb(1)–C(1)	2.151(5)	Sb(1)–C(1)	2.156(8)
Sb(1)–C(10)	2.156(3)	Sb(1)–C(10)	2.1679(15)	Sb(1)–C(14)	2.147(6)	Sb(1)–C(14)	2.131(8)
Sb(1)–N(1)	2.393(3)	Sb(1)–N(1)	2.5454(13)	Sb(1)–N(1)	2.409(4)	Sb(1)–N(1)	2.324(6)
Sb(1)···N(2)	3.219(3)						
Sb(1)–O(1)	2.375(3)	Sb(1)–O(1)	2.0790(13)	Sb(1)–Cl(1)	2.5133(18)	Sb(1)–O(1)	2.304(5)
Sb(1)···O(3)	3.145(3)						
N(3)–O(1)	1.259(5)	S(1)–O(2)	1.4463(12)			S(1)–O(1)	1.472(6)
N(3)–O(2)	1.217(5)	S(1)–O(3)	1.4364(13)			S(1)–O(2)	1.421(9)
N(3)–O(3)	1.239(5)	S(1)–O(4)	1.4374(13)			S(1)–O(3)	1.411(7)
		O(1)-H(1)	0.731(18)				
		O(2)···H(1)	2.142(18)				
		O(1)···O(2)	2.871(2)				
		N(2)-H(2)	1.000(0)				
		O(1)···H(2)	1.600				
		N(2)···O(1)	2.591(2)				
O(1)–Sb(1)–N(1)	158.49(9)	O(1)–Sb(1)–N(1)	159.65(4)	Cl(1)–Sb(1)–N(1)	160.31(9)	O(1)–Sb(1)–N(1)	153.5(2)
C(1)–Sb(1)···N(2)	148.23(11)	C(1)–Sb(1)···N(2)					
C(1)–Sb(1)–C(10)	96.99(14)	C(1)–Sb(1)–C(10)	104.35(6)	C(1)–Sb(1)–C(14)	98.5(2)	C(1)–Sb(1)–C(14)	104.2(3)
C(10)–Sb(1)–N(1)	96.03(12)	C(10)–Sb(1)–N(1)	86.14(5)	C(14)–Sb(1)–N(1)	76.60(16)	C(14)–Sb(1)–N(1)	76.6(2)
C(10)–Sb(1)···N(2)	65.74(11)	C(10)–Sb(1)···N(2)					
C(10)–Sb(1)–O(1)	85.27(12)	C(10)–Sb(1)–O(1)	86.89(5)	C(14)–Sb(1)–Cl(1)	92.17(14)	C(10)–Sb(1)–O(1)	86.5(2)
C(1)–Sb(1)–N(1)	76.24(12)	C(1)–Sb(1)–N(1)	73.25(5)	C(1)–Sb(1)–N(1)	74.31(16)	C(1)–Sb(1)–N(1)	77.7(3)
N(1)–Sb(1)···N(2)	79.26(8)	N(1)–Sb(1)···N(2)					
N(2)···Sb(1)–O(1)	120.20(9)	N(2)···Sb(1)–O(1)					
C(1)–Sb(1)–O(1)	82.29(12)	C(1)–Sb(1)–O(1)	90.03(5)	C(1)–Sb(1)–Cl(1)	91.77(14)	C(1)–Sb(1)–O(1)	87.0(3)
O(1)–N(3)–O(2)	119.0(3)	O(2)–S(1)–O(3)	114.46(7)			O(1)–S(1)–O(2)	112.7(4)
O(1)–N(3)–O(3)	118.8(3)	O(2)–S(1)–O(4)	114.74(7)			O(1)–S(1)–O(3)	113.1(4)
O(2)–N(3)–O(3)	122.2(4)	O(3)–S(1)–O(4)	115.46(7)			O(2)–S(1)–O(3)	118.4(4)
		O(1)-H(1)···O(2)	176.7(16)				
		N(2)-H(2)···O(1)	168.00				

dimers, i.e. (pS^1,pS^2)-**4a**/(pS^1,pS^2)-**4b** and (pR^1,pR^2)-**4a**/(pR^1,pR^2)-**4b**, respectively, based on C–H···π (Ar$_{centroid}$) contacts (C(15)–H(15A)$_{methylene}$···Ph$_{centroid}${C(37)–C(42)} 2.65 Å, $\gamma = 5.3°$; C(36)–H(36A)$_{methylene}$···Ar$_{centroid}${C(9)–C(14)} 2.87 Å, $\gamma = 12.7°$). Such dimers form tetranuclear units through further C–H···π (Ar$_{centroid}$) contacts (C(10)–H(10)$_{aryl}$···Ar$_{centroid}${C(30′)–C(35′)} 2.83 Å, $\gamma = 13.6°$) (see Figures S8 and S9 in the supporting information). Finally, a complex three-dimensional supramolecular architecture is constructed from the tetranuclear units connected by additional C–H···π (Ar$_{centroid}$) and C–H···Cl contacts (for details, see Figure S10 in the supporting information).

The molecules of **6** are double bridged through C–H···π (Ar$_{centroid}$) contacts (C(4)–H(4)$_{aryl}$···Ar$_{centroid}${C(9b)–C(14b)} 2.75 Å, $\gamma = 8.4°$; C(8)–H(8B)$_{methylene}$···Ar$_{centroid}${C(9a)–C(14a)} 2.70 Å, $\gamma = 5.6°$) into a chain of alternating (pS^1,pS^2)-**6** and (pR^1,pR^2)-**6** isomers (see Figure S11 in the supporting information). Layers are formed from parallel chains based on C–H···O contacts (C(12)–H(12)$_{aryl}$···O(3′) 2.50 Å) (for details, see Figure S12 in the supporting information).

3.4 | Catalytic results

Table 2 summarizes catalytic results for the Henry addition of nitromethane to benzaldehyde performed at 50°C or at room temperature, over hypercoordinated organoantimony(III) compounds, as well as theoretical calculated total atomic charge on antimony and on the weakest coordinated nitrogen. Both the proligands and Ph_3Sb showed either no activity or a very small one.

However, the amine $Me_2NCH_2C_6H_5$ provided a small selectivity into the nitroaldol. For the diorganoantimony(III) complexes **1–6**, a more positively charged antimony coupled with a more negatively charged nitrogen had a direct influence on the increase of the activity (catalysts **2**, **3** and **6**) providing a complete conversion of the benzaldehyde. On the other hand, a decrease of the positive charge on antimony (catalysts **1**, **4** and **5**) favours dehydration of 1-hydroxy-2-nitroethylbenzene to 2-nitrostyrene. It results that the positive effect of the anion decreases in the following order: $OSO_2CF_3 > ONO_2 > Cl$. Of note, the activity of catalyst **3** corresponds to a turnover number of around 1.5×10^6, which is indeed a very high value.

Additional experiments were carried out at room temperature with the most effective catalysts **2** and **3** and they showed no decrease in both the conversion of benzaldehyde and the selectivity to nitroaldol. Furthermore, experiments with different loadings of catalysts were also carried out with these two compounds. At room temperature, a five-fold reduction of the loading of **2** led to a decrease of the conversion of the benzaldehyde to 94.6% with no change in the selectivity, while for catalyst **3**, under similar experimental conditions, no change of the conversion or selectivity was observed. The selectivity was preserved also by working with different benzaldehyde/nitromethane/catalyst ratios, but the conversion decreased to 97.8% and 91.7%, respectively, for 0.5/100 and 15/70 millimolar benzaldehyde/nitromethane ratios with a loading of 0.01 mmol of catalyst **3**.

4 | CONCLUSIONS

Two types of hypercoordinated diorganoantimony(III) compounds, namely **2** and **3**, bearing two aromatic groups with pendant arms capable of N→Sb intramolecular interactions, and **5** and **6**, based on a butterfly-like tetrahydrodibenzo[*c*,*f*][1,5]-azastibocine heterocyclic framework with a N→Sb transannular interaction, were prepared,

TABLE 2 Catalytic results for the Henry addition of nitromethane over hypercoordinated organoantimony(III) compounds

Catalyst (solubility)	Positive charge on Sb/negative charge on N	Conversion of benzaldehyde (%)	Selectivity (%)	
			Nitroaldol	Nitroalkene
1 (water soluble)	0.835/−0.208	91.3	70.2	29.8
2(water soluble)	0.939/−0.211	100	100	0
2^a(water soluble)	0.939/−0.211	100	100	0
2^b(water soluble)	0.939/−0.211	94.6	100	0
3(water soluble)	0.949/−0.231	100	100	0
3^a(water soluble)	0.949/−0.231	100	100	0
3^b(water soluble)	0.949/−0.231	100	100	0
3^c(water soluble)	0.949/−0.231	91.7	100	0
4(no solubility in water)	0.819/−0.229	89.3	66.8	33.2
5(no solubility in water)	0.911/−0.222	94.8	71.8	28.2
6(no solubility in water)	0.932/−0.215	100	84.5	15.5
7$[2\text{-}(Me_2NCH_2)C_6H_4]SbCl_2$ (no solubility in water)		0	0	0
8Ph_3Sb (no solubility in water)		0	0	0
9$Me_2NCH_2C_6H_5$ (water soluble)		29.7	6.5	93.5
10$PhCH_2N(CH_2C_6H_4Br\text{-}2)_2$ (water soluble)		0	0	0

Reaction conditions: 0.5 mmol benzaldehyde, 10 mmol nitromethane, 3 ml water, 0.05 mmol catalyst (for entries 6 and 7: 0.0176 g catalyst), 50°C, 24 h.

[a] Room temperature, 0.05 mmol catalyst.

[b] Room temperature, 0.01 mmol catalyst.

[c] 15 mmol benzaldehyde, 70 mmol nitromethane, 3 ml water, room temperature, 0.01 mmol catalyst.

structurally characterized and investigated as catalysts in the Henry (nitroaldol) reaction. The ^{1}H NMR spectra gave no clear evidence for the N→Sb intramolecular coordination in solution, while the single-crystal X-ray diffraction studies evidenced two N→Sb intramolecular interactions of different strengths (2.393(3)/3.219 Å) in **2**, and only a strong one (2.5454(12) Å) in the hydrolysis product **3h**, in which the nitrogen atom in the second pendant arm is pushed far away from the coordination sphere of antimony. In the azastibocine derivatives **4** and **6**, strong transannular N→Sb interactions were also observed. The NO_3^- ligand in **2** and the $CF_3SO_3^-$ ligand in **6** act as bidentate moieties, thus resulting in hexa-coordinated and penta-coordinated antimony, respectively, while in **3h** and **4** antimony is tetrahedrally surrounded by the donor atoms. The catalytic experiments have shown that a more positively charged antimony coupled with a more negatively charged nitrogen had a direct influence on the increase of the activity (catalysts **2**, **3** and **6**), thus providing a complete conversion of benzaldehyde. The decrease of the positive charge on the metal centre (catalysts **1**, **4** and **5**) favours dehydration of 1-hydroxy-2-nitroethylbenzene to 2-nitrostyrene. For **2** and **3**, it was observed that the catalytic activity was not affected by temperature in the range 23–50°C. The combination of the 2-(Me_2NCH_2)C_6H_4 substituent on antimony with either nitrate or triflate anions provides the most efficient catalysts with turnover numbers of the order of 10^6.

ACKNOWLEDGMENTS

This work was supported through a grant of Ministery of Research and Innovation, National University Research Council of Romania, CNCS-UEFISCDI, project number PN-III-P4-ID-PCE-2016-0857, within PNCDI III. The support provided by the National Centre for X-Ray Diffraction (Babes-Bolyai University, Cluj-Napoca, Romania) for XRD determinations and refinement is gratefully acknowledged. Theoretical calculations were performed on the high-performance computational facility MADECIP, POSCCE, COD SMIS 48801/1862 co-financed by the European Regional Development Fund of the European Union.

ORCID

Ciprian I. Raţ https://orcid.org/0000-0002-1154-8130
Anca Sivestru https://orcid.org/0000-0002-0942-581X

REFERENCES

[1] (a) N. Tan, Y. Chen, S. Yin, R. Qiu, Y. Zhou, C. T. Au, *Curr. Org. Chem.* **2012**, *16*, 2462. (b) C. I. Raţ C. Silvestru, H. J. Breunig, *Coord. Chem. Rev.* **2013**, *257*, 818.

[2] C. W. Perkins, J. C. Martin, A. J. Arduengo III, W. Lau, A. Alegria, J. K. Kochi, *J. Am. Chem. Soc.* **1980**, *102*, 7753.

[3] (a) S. Kamepalli, C. J. Carmalt, R. D. Culp, A. H. Cowley, R. A. Jones, N. C. Norman, *Inorg. Chem.* **1996**, *35*, 6179. (b) C. J. Carmalt, D. Walsh, A. H. Cowley, N. C. Norman, *Organometallics* **1997**, *16*, 3597. (c) C. J. Carmalt, A. H. Cowley, R. D. Culp, R. A. Jones, S. Kamepalli, N. C. Norman, *Inorg. Chem.* **1997**, *36*, 2770. (d) T. Tokunaga, H. Seki, S. Yasuike, M. Ikoma, J. Kurita, K. Yamaguchi, *Tetrahedron Lett.* **2000**, *41*, 1031. (e) T. Tokunaga, H. Seki, S. Yasuike, M. Ikoma, J. Kurita, K. Yamaguchi, *Tetrahedron* **2000**, *56*, 8833. (f) S. Okajima, S. Yasuike, N. Kakusawa, A. Osada, K. Yamaguchi, H. Seki, J. Kurita, *J. Organometal. Chem.* **2002**, *656*, 234. (g) H. J. Breunig, I. Ghener, M. E. Ghener, E. Lork, *Inorg. Chem.* **2003**, *42*, 1751. (h) L. M. Opri, A. Silvestru, C. Silvestru, H. J. Breunig, E. Lork, *Dalton Trans.* **2003**, 4367. (i) L. M. Opri, A. Silvestru, C. Silvestru, H. J. Breunig, E. Lork, *Dalton Trans.* **2004**, 3575. (j) P. Sharma, D. Castillo, N. Rosas, A. Cabrera, E. Gomez, A. Toscano, F. Lara, S. Hernandez, G. Espinosa, *J. Organometal. Chem.* **2004**, *689*, 2593. (k) L. M. Opri, A. M. Preda, R. A. Varga, H. J. Breunig, C. Silvestru, *Eur. J. Inorg. Chem.* **2009**, *2009*, 1187. (l) H. J. Breunig, E. Lork, O. Moldovan, C. I. Ra, U. Rosenthal, C. Silvestru, *Dalton Trans.* **2009**, 5065. (m) M. Olaru, S. Roca, C. I. Ra, C. Silvestru, *Acta Crystallogr. E* **2009**, *E65*, m1383. (n) D. Copolovici, V. R. Bojan, C. I. Ra, A. Silvestru, H. J. Breunig, C. Silvestru, *Dalton Trans.* **2010**, *39*, 6410. (o) A. P. Soran, V. R. Bojan, *Acta Crystallogr. E* **2010**, *E66*, m423. (p) H. J. Breunig, E. Lork, O. Moldovan, C. I. Ra, *Z. Anorg. Allg. Chem.* **2010**, *636*, 1090. (q) H. Yamamichi, S. Matsukawa, S. Kojima, K. Ando, Y. Yamamoto, *Heteroat. Chem.* **2011**, *22*, 553. (r) M. Barsukova-Stuckart, L. F. Piedra-Garza, B. Gautam, G. Alfaro-Espinoza, N. V. Izarova, A. Banerjee, B. S. Bassil, M. S. Ullrich, H. J. Breunig, C. Silvestru, U. Kortz, *Inorg. Chem.* **2012**, *51*, 12015. (s) A. Toma, C. I. Raţ, A. Silvestru, T. Rüffer, H. Lang, M. Mehring, *J. Organometal. Chem.* **2013**, *745-746*, 71. (t) D. Copolovici, F. Isaia, H. J. Breunig, C. I. Raţ C. Silvestru, *RSC Adv.* **2014**, *4*, 26569. (u) A. M. Preda, C. I. Raţ, C. Silvestru, H. Lang, T. Rüffer, M. Mehring, *RSC Adv.* **2015**, *5*, 99832. (v) P. Yang, Z. Lin, G. Alfaro-Espinoza, M. S. Ullrich, C. I. Raţ, C. Silvestru, U. Kortz, *Inorg. Chem.* **2016**, *55*, 251.

[4] I. Chircă, C. Silvestru, H. J. Breunig, C. I. Raţ, *Inorg. Chim. Acta* **2018**, *475*, 155.

[5] I. Chircă, A. Soran, A. Silvestru, C. Silvestru, *Rev. Roum. Chim.* **2015**, *60*, 643.

[6] D. Copolovici, C. Silvestru, R. A. Varga, *Acta Crystallogr. C* **2008**, *C64*, m37.

[7] A. M. Preda, C. I. Raţ, C. Silvestru, H. J. Breunig, H. Lang, T. Rüffer, M. Mehring, *Dalton Trans.* **2013**, *42*, 1144.

[8] (a) M. Jura, W. Levason, G. Reid, M. Webster, *Dalton Trans.* **2009**, 7811. (b) S. L. Benjamin, W. Levason, G. Reid, M. C. Rogers, *Dalton Trans.* **2011**, *40*, 6565. (c) S. L. Benjamin, W. Levason, G. Reid, *Organometallics* **2013**, *32*, 2760.

[9] (a) D. A. Atwood, A. H. Cowley, J. Ruiz, *Inorg. Chim. Acta* **1992**, *198-200*, 271. (b) Y. Yamamoto, X. Chen, S. Kojima, K. Ohdoi, M. Kitano, Y. Doi, K.-Y. Akiba, *J. Am. Chem. Soc.* **1995**, *117*, 3922. (c) L. Dostál, R. Jambor, A. Růžička,

J. Holeček, *Organometallics* **2008**, *27*, 2169. (d) L. Dostál, R. Jambor, A. Růžička, A. Lyčka, J. Brus, F. de Proft, *Organometallics* **2008**, *27*, 6059. (e) L. Dostál, R. Jambor, A. Růžička, R. Jirásko, I. Císařová, J. Holeček, *J. Fluorine Chem.* **2008**, *129*, 167. (f) L. Dostál, R. Jambor, A. Růžička, M. Erben, R. Jirásko, E. Černošková, J. Holeček, *Organometallics* **2009**, *28*, 2633. (g) A. Fridrichová, T. Svoboda, R. Jambor, Z. Padělková, A. Růžička, M. Erben, R. Jirásko, L. Dostál, *Organometallics* **2009**, *28*, 5522. (h) L. Dostál, R. Jambor, A. Růžička, R. Jirásko, V. Lochař, L. Beneš, F. de Proft, *Inorg. Chem.* **2009**, *48*, 10495. (i) L. Dostál, R. Jambor, A. Růžička, R. Jirásko, E. Černošková, L. Beneš, F. de Proft, *Organometallics* **2010**, *29*, 4486. (j) T. Svoboda, R. Jambor, A. Růžička, Z. Padělková, M. Erben, R. Jirásko, L. Dostál, *Eur. J. Inorg. Chem.* **2010**, *2010*, 1663. (k) T. Svoboda, R. Jambor, A. Růžička, Z. Padělková, M. Erben, L. Dostál, *Eur. J. Inorg. Chem.* **2010**, *2010*, 5222. (l) T. Svoboda, L. Dostál, R. Jambor, A. Růžička, R. Jirásko, A. Lyčka, *Inorg. Chem.* **2011**, *50*, 6411. (m) T. Svoboda, R. Jambor, A. Růžička, R. Jirásko, A. Lyčka, F. de Proft, L. Dostál, *Organometallics* **2012**, *31*, 1725. (n) T. Řezníček, L. Dostál, A. Růžička, J. Vinklárek, M. Řezáčová, R. Jambor, *Appl. Organometal. Chem.* **2012**, *26*, 237. (o) A. Fridrichová, B. Mairychová, Z. Padělková, A. Lyčka, K. Jurkschat, R. Jambor, L. Dostál, *Dalton Trans.* **2013**, *42*, 16403. (p) B. Mairychová, T. Svoboda, P. Štěpnička, A. Růžička, R. W. A. Havenith, M. Alonso, F. de Proft, R. Jambor, L. Dostál, *Inorg. Chem.* **2013**, *52*, 1424. (q) B. Mairychová, T. Svoboda, M. Erben, A. Růžička, L. Dostál, R. Jambor, *Organometallics* **2013**, *32*, 157. (r) M. Kořenková, M. Erben, R. Jambor, A. Růžička, L. Dostál, *J. Organometal. Chem.* **2014**, *772–773*, 287. (s) M. Kořenková, B. Mairychová, A. Růžička, R. Jambor, L. Dostál, *Dalton Trans.* **2014**, *43*, 7096. (t) R. Kather, T. Svoboda, M. Wehrhahn, E. Rychagova, E. Lork, L. Dostál, S. Ketkov, J. Beckmann, *Chem. Commun.* **2015**, *51*, 5932. (u) L. Dostál, R. Jambor, A. Růžička, R. Jirásko, A. Lyčka, J. Beckmann, S. Ketkov, *Inorg. Chem.* **2015**, *54*, 6010. (v) R. Jambor, Z. A. Růžičková, M. Erben, L. Dostál, *Inorg. Chem. Commun.* **2017**, *76*, 36.

[10] G. Strîmb, A. Pöllnitz, C. I. Raţ, C. Silvestru, *Dalton Trans.* **2015**, *44*, 9927.

[11] (a) L. Dostál, I. Císařová, R. Jambor, A. Růžička, R. Jirásko, J. Holeček, *Organometallics* **2006**, *25*, 4366. (b) L. Dostál, P. Novák, R. Jambor, A. Růžička, I. Císařová, R. Jirásko, J. Holeček, *Organometallics* **2007**, *26*, 2911. (c) L. Dostál, R. Jambor, I. Císařová, L. Beneš, A. Růžička, R. Jirásko, J. Holeček, *J. Organometal. Chem.* **2007**, *692*, 2350. (d) M. Chovancová, R. Jambor, A. Růžička, R. Jirásko, I. Císařová, L. Dostál, *Organometallics* **2009**, *28*, 1934.

[12] (a) L. Machuca, L. Dostál, R. Jambor, K. Handlíř, R. Jirásko, A. Růžička, I. Císařová, J. Holeček, *J. Organometal. Chem.* **2007**, *692*, 3969. (b) L. Dostál, R. Jambor, A. Růžička, I. Císařová, J. Holeček, *Inorg. Chim. Acta* **2010**, *363*, 1607. (c) L. Dostál, R. Jambor, A. Růžička, R. Jirásko, J. Holeček, F. de Proft, *Dalton Trans.* **2011**, *40*, 8922.

[13] (a) J. Vrána, R. Jambor, A. Růžička, J. Holeček, L. Dostál, *Collect. Czech. Chem. Commun.* **2010**, *75*, 1041. (b) J. Vrána, R. Jambor, A. Růžička, A. Lyčka, L. Dostál, *J. Organometal. Chem.* **2012**, *718*, 78.

[14] (a) N. Kakusawa, Y. Tobiyasu, S. Yasuike, K. Yamaguchi, H. Seki, J. Kurita, *Tetrahedron Lett.* **2003**, *44*, 8589. (b) N. Kakusawa, Y. Tobiyasu, S. Yasuike, K. Yamaguchi, H. Seki, J. Kurita, *J. Organometal. Chem.* **2006**, *691*, 2953.

[15] (a) N. Kakusawa, J. Kurita, *Heterocycles* **2006**, *68*, 1335. (b) N. Kakusawa, S. Yasuike, J. Kurita, *Heterocycles* **2009**, *77*, 1269. (c) N. Kakusawa, S. Yasuike, J. Kurita, *Heterocycles* **2010**, *80*, 163. (d) Y. Chen, K. Yu, N.-Y. Tan, R.-H. Qiu, W. Liu, N.-L. Luo, L. Tong, C.-T. Au, Z.-Q. Luo, S.-F. Yin, *Eur. J. Med. Chem.* **2014**, *79*, 391.

[16] (a) J. Xia, R. Qiu, S. Yin, X. Zhang, S. Luo, C.-T. Au, K. Xia, W.-Y. Wong, *J. Organometal. Chem.* **2010**, *695*, 1487. (b) W. Yi, N. Tan, *Acta Crystallogr. E* **2011**, *E67*, m917.

[17] N. Tan, T. Nie, C.-T. Au, D. Lan, S. Wu, B. Yi, *Tetrahedron Lett.* **2017**, *58*, 2592.

[18] N. Tan, D. Lan, S. Wu, C.-T. Au, B. Yi, *Z. Kristallogr. New Cryst. Struct.* **2018**, *233*, 679.

[19] N. Tan, Y. Chen, S.-F. Yin, R. Qiu, Y. Zhou, C.-T. Au, *Dalton Trans.* **2013**, *42*, 9476.

[20] L. Henry, *Bull. Soc. Chim. Fr.* **1895**, *13*, 999.

[21] (a) J. Boruwa, N. Gogoi, P. P. Saikia, N. C. Barua, *Tetrahedron: Asymmetry* **2006**, *17*, 3315. (b) A. Majhi, S. T. Kadam, S. S. Kim, *Bull. Korean Chem. Soc.* **2009**, *30*, 1767. (c) P. Sakthipriya, S. Joseph, N. Ananthi, *MOJ Biorg. Org. Chem* **2017**, *1*(6), 218.

[22] F. H. Carré, R. J. P. Corriu, G. F. Lanneau, P. Merle, F. Soulairol, J. Yao, *Organometallics* **1997**, *16*, 3878.

[23] MestReC and MestReNova, Mestrelab Research SL, Santiago de Compostela, Spain. **2015**.

[24] G. M. Sheldrick, *Acta Crystallogr. C* **2015**, *C71*, 3.

[25] L. J. Farrugia, *J. Appl. Crystallogr.* **2012**, *45*, 849.

[26] (a) A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7. (b) A. L. Spek, *Acta Crystallogr. D* **2009**, *D65*, 148.

[27] DIAMOND – Visual Crystal Structure Information System, Crystal Impact, Bonn, Germany. **2015**.

[28] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09, Revision E.01*, Gaussian Inc., Wallingford, CT **2013**.

[29] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.

[30] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

[31] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456.

[32] M. Iwaoka, S. Tomoda, *J. Am. Chem. Soc.* **1996**, *118*, 8077.

[33] A. M. Toma, A. Pop, A. Silvestru, T. Rüffer, H. Lang, M. Mehring, *Dalton Trans.* **2017**, *46*, 3953.

[34] (a) K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds – Part B*, 6th ed., John Wiley, Hoboken, NJ **2009** 92. (b) H. J. Breunig, M. G. Nema, C. Silvestru, A. P. Soran, R. A. Varga, *Dalton Trans.* **2010**, *39*, 11277.

[35] (a) P.-Å. Bergström, J. Lindgren, *J. Mol. Struct.* **1990**, *239*, 103. (b) S. P. Gejji, K. Hermansson, J. Lindgren, *J. Phys. Chem.* **1993**, *97*, 3712.

[36] J. Emsley, *Die Elemente*, Walter de Gruyter, Berlin **1994**.

[37] IUPAC, *Nomenclature of Organic chemistry*, Pergamon Press, Oxford **1979**.

[38] N. G. Connelly, T. Damhus, R. M. Hartshorn, A. T. Hutton (Eds), *Nomenclature of Inorganic Chemistry: IUPAC Recommendations 2005*, RSC Publishing, Cambridge **2005**.

[39] M. Nishio, *Phys. Chem. Chem. Phys.* **2011**, *13*, 13873.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

How to cite this article: Şuteu R, Raţ CI, Sivestru C, et al. Hypercoordinated diorganoantimony(III) compounds of types [2-$(Me_2NCH_2)C_6H_4]_2$SbL and $[PhCH_2N(CH_2C_6H_4)_2]$SbL (L = Cl, ONO_2, OSO_2CF_3). Synthesis, structure and catalytic behaviour in the Henry reaction. *Appl Organometal Chem*. 2020;e5393. https://doi.org/10.1002/aoc.5393