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Synthesis and Characterization of Hypervalent Organoantimony(III) Compounds Containing the $[2\text{-}(Me_2NCH_2)C_6H_4]_2Sb$ Fragment

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Compounds containing the $[2\text{-}(Me_2NCH_2)C_6H_4]_2Sb$ moiety were prepared by using R_2SbX [X = Cl (**1**), Br (**2**)] as starting materials. The reaction of **1** with Me_3SiCH_2MgCl gave the mixed alkyl–aryl stibine $R_2SbCH_2SiMe_3$ (**3**). Reduction of **2** with Mg in thf followed by in situ air oxidation or treatment with S_8 resulted in the isolation of $(R_2Sb)_2E$ [E = O (**4**), S (**5**)]. Compound **5** is also formed from R_2SbCl and Na_2S. The reaction of **4** with $[W(CO)_5(thf)]$ gives the unexpected complex $[(R_2SbOH)W(CO)_5]$ (**6**). The new compounds were investigated by IR, ^1H, and ^{13}C NMR spectroscopy, as well as by mass spectrometry. The structures of **3**–**6** were determined by single-crystal X-ray diffraction. For compounds **3**–**5**, both nitrogen atoms from the pendant arms are involved in intramolecular N→Sb coordination, which results in distorted square-pyramidal $(C,N)_2SbC$ or $(C,N)_2SbE$ (E = O, S) cores. By contrast, in **6** only one nitrogen atom is strongly coordinated to the antimony center, whereas the second nitrogen atom is involved in N···H–O bonding.

Introduction

The chemistry of organoantimony compounds containing the $[2\text{-}(Me_2NCH_2)C_6H_4]$ group has developed considerably during the last years.[1–11] This organic moiety was shown to be able to behave as a C,N ligand, which thus allowed the isolation of unusual hypervalent organoantimony species, such as the first chalcogeno-bridged compounds of the type $(RSbX)_2E$ (X = halogen, E = O, S),[9] the air-stable heterocyclic $(RSbS)_2$, or the complex *cis*-cyclo-$[(RSbS)_2W(CO)_5]$ with an *S*-coordinated metalcarbonyl fragment.[10] It should be noted that in the asymmetric alkali metal diorganoantimonides $R[(Me_3Si)_2CH]SbLi\cdot 2thf$ and $R[(Me_3Si)_2CH]SbNa\cdot tmeda$ [R = $2\text{-}(Me_2NCH_2)C_6H_4$] the nitrogen atom of the pendant arm interacts with the alkali metal atom rather than the antimony center.[8] Compounds with more than one 2-(dimethylaminomethyl)-phenyl group have been rather sparingly investigated. Besides the halides R_2SbX (X = Cl, Br, I),[5,9] R_3Sb,[3,11] and some of their adducts with HX,[9,11] only a few other compounds were reported, that is, the ionic derivatives $[R_2Sb]^+[PF_6]^-$[4] and $[R_3SbOH]^+[I_3]^-$[9] and the complex $[Pt(SbR_3)Cl_2]$.[11]

With the aim to develop the chemistry of compounds containing two 2-(dimethylaminomethyl)phenyl groups attached to antimony, we report here on the synthesis and structural characterization in solution and the solid state of $[2\text{-}(Me_2NCH_2)C_6H_4]_2SbCH_2SiMe_3$ (**3**), $[\{2\text{-}(Me_2NCH_2)\text{-}C_6H_4\}_2Sb]_2E$ [E = O (**4**), S (**5**)], and the first hypervalent diorganoantimony(III) hydroxide metalcarbonyl complex $[(\{2\text{-}(Me_2NCH_2)C_6H_4\}_2SbOH)W(CO)_5]$ (**6**). It should be noted that the molecular structure of only a few uncomplexed compounds of the type $(R_2Sb)_2O$ (R = Me,[12] Ph,[13,14] *o*-tolyl, *p*-tolyl[14]) and $(Me_2Sb)_2S$[12] have been described so far.

Results and Discussion

The mixed alkyl–aryl stibine $[2\text{-}(Me_2NCH_2)C_6H_4]_2\text{-}SbCH_2SiMe_3$ (**3**) was obtained by treating Me_3SiCH_2MgCl with R_2SbCl (**1**) in thf. Reduction of the monobromide R_2SbBr (**2**) with Mg in thf gave the distibane $R_2Sb\text{–}SbR_2$, which was converted in situ into $(R_2Sb)_2E$ [E = O (**4**), S (**5**)] by air oxidation or treatment with elemental sulfur, respectively. Sulfide **5** was also obtained in high yield from R_2SbCl and an excess amount of Na_2S in water/toluene. Treatment of oxide **4** with $[W(CO)_5(thf)]$ followed by work up of the reaction mixture in open atmosphere afforded the unexpected complex $[(R_2SbOH)W(CO)_5]$ (**6**) in rather high yield (ca. 50%) (Scheme 1). This behavior is in contrast to the previous reports that described the potential of some $(R_2Sb)_2E$ chalcogenides to act as terminal[15] or bridging[15–18] ligands in transition-metal complexes.

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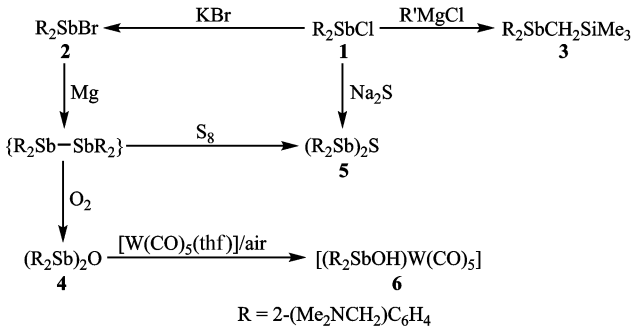


Scheme 1.

The compounds were obtained as air-stable, colorless (**3**, **4**), yellow (**5**), or orange (**6**) crystalline solids that melt without decomposition. They are soluble in common organic solvents, such as chloroform, benzene, or toluene. MS and NMR spectroscopic data of **3**–**6** as well as elemental analytical data are consistent with the anticipated formulas. Characteristic ions, including the molecular ion, are present in the mass spectra, which always contain [$(Me_2NCH_2C_6H_4)_2$-Sb^+] as the base peak. The IR spectra indicated the presence of the $W(CO)_5$ moiety in complex **6**.

Solid-State Structures

Single crystals suitable for X-ray diffraction studies were obtained by slow diffusion of *n*-hexane into a $CHCl_3$ solution of compounds **3**–**5**, or by cooling a concentrated toluene solution of **6** at –28 °C. The molecular structures are shown in Figures 1, 2, and 3, and selected interatomic distances and angles are listed in Table 1.

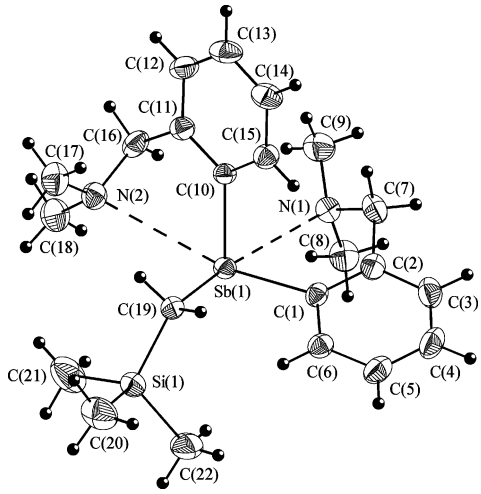
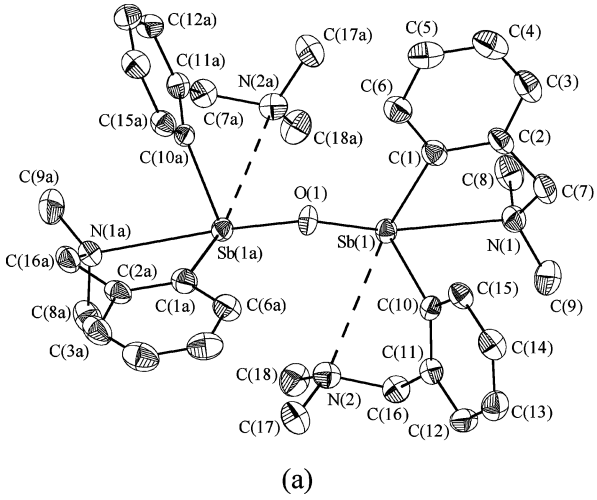


Figure 1. ORTEP representation at 30% probability and atom numbering scheme for ($R_{N1}S_{N2}$)-**3** (for R_{N1} and S_{N2} abbreviations, see the text).

A common feature for compounds **3**–**5** is that the nitrogen atoms of the pendant Me_2NCH_2 arm from both organic groups establish internal N→Sb interactions of different strengths. In **3**, the N(1) atom coordinates stronger in the *trans* position to the C(sp^3) atom of the of the CH_2SiMe_3 group [Sb(1)–N(1) 2.971(3) Å, N(1)–Sb(1)–C(19) 161.32(12)°], whereas the N(2) atom exhibits a weaker interaction in the *trans* position to the C(sp^2) atom of the other aromatic substituent [Sb(1)–N(2) 3.189(3) Å, N(2)–Sb(1)–C(1) 160.73(12)°]. In chalcogenides **4** and **5**, the intramolecular N→Sb interaction established *trans* to the chalcogen atom is much stronger [Sb(1)–N(1) 2.775(5) Å, N(1)–Sb(1)–O(1) 159.82(10)° in **4**; Sb(1)–N(1) 2.855(3) Å, N(1)–Sb(1)–S(1) 152.41(6)° in **5**], consistent with the higher electronegativity of the *trans* atom. The nitrogen atom of



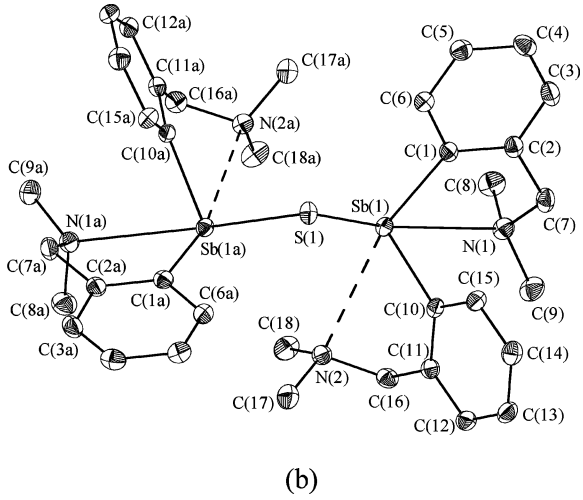


Figure 2. ORTEP representation at 30% probability and atom numbering scheme for (a) (R_{N1},S_{N2}/R_{N1a},S_{N2a})-**4** [symmetry equivalent atoms (1 – *x*, *y*, 0.5 – *z*) are denoted with an "a"] and (b) (S_{N1},R_{N2}/S_{N1a},R_{N2a})-**5** [symmetry equivalent atoms (–*x*, *y*, 0.5 – *z*) are denoted with an "a"]. Hydrogen atoms are omitted.

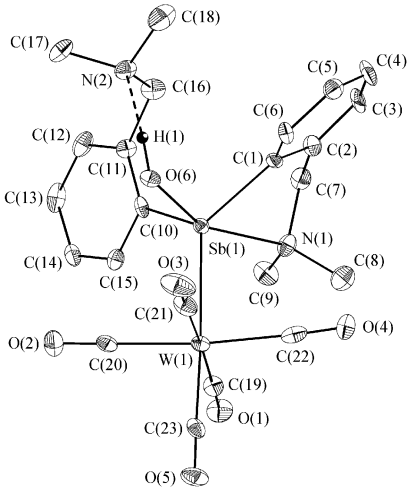


Figure 3. ORTEP representation at 30% probability and atom numbering scheme for ($R_{N1}A_{Sb}$)-**6** (for R_{N1} and A_{Sb} abbreviations, see the text). Hydrogen atoms, other than that of the hydroxy group, are omitted.

Table 1. Selected bond lengths [Å] and angles [°] for compounds **3**–**6**.

	3	**4**	**5**	**6**
Sb(1)–C(1)	2.184(4)	2.158(5)	2.190(4)	2.112(8)
Sb(1)–C(10)	2.159(4)	2.160(5)	2.169(3)	2.151(9)
Sb(1)–E(1)[a]	2.169(4)	1.986(3)	2.4621(10)	1.976(7)
Sb(1)–N(1)	2.971(3)	2.775(5)	2.855(3)	2.860(9)
Sb(1)–N(2)	3.189(3)	3.240(4)	3.025(3)	3.740(9)[b]
Sb(1)–W(1)				2.7513(11)
O(6)–H(1)				0.94(10)
N(2)–H(1)				1.99(10)
C(1)–Sb(1)–C(10)	96.04(14)	95.29(19)	95.89(13)	110.3(3)
E(1)–Sb(1)–C(1)	94.71(14)	89.90(18)	92.03(10)	92.6(3)
E(1)–Sb(1)–C(10)	94.26(14)	95.85(15)	95.14(9)	94.9(3)
N(1)–Sb(1)–C(1)	68.85(12)	70.55(17)	70.34(11)	69.1(3)
N(1)–Sb(1)–C(10)	79.32(12)	81.40(16)	76.82(11)	79.8(3)
N(1)–Sb(1)–E(1)	161.32(12)	159.82(10)	152.41(6)	157.3(3)
N(1)–Sb(1)–N(2)	112.56(8)	112.77(11)	104.18(8)	
N(2)–Sb(1)–C(1)	160.73(12)	157.85(17)	163.89(11)	
N(2)–Sb(1)–C(10)	66.17(12)	64.62(13)	68.01(11)	
N(2)–Sb(1)–E(1)	79.92(12)	83.40(8)	89.85(6)	
Sb(1)–E(1)–Sb(1a)		115.9(3)	100.78(5)	
Sb(1)–O(6)–H(1)				112(6)
W(1)–Sb(1)–C(1)				126.8(2)
W(1)–Sb(1)–C(10)				118.7(2)
W(1)–Sb(1)–O(6)				102.27(19)
W(1)–Sb(1)–N(1)				99.6(2)
O(6)–H(1)–N(2)				157(8)

[a] E(1) = C(19) for **3**, O(1) for **4**, S(1) for **5**, and O(6) for **6**. [b] Nonbonding distance.

the other amine group exhibits a weaker intramolecular interaction, and its vector lies approximately *trans* to a carbon atom [Sb(1)–N(2) 3.240(4) Å, N(2)–Sb(1)–C(1) 157.85(17)° in **4**; Sb(1)–N(2) 3.025(3) Å, N(2)–Sb(1)–C(1) 163.89(11)° in **5**]. The strength of the Sb(1)–N(1) interaction *trans* to the chalcogen atom is considerably smaller than that in the monohalides $[2\text{-}(Me_2NCH_2)C_6H_4]_2SbX$ [2.463(2), 2.423(3), and 2.417(3) Å for X = Cl,[5] Br, and I,[9] respectively], which contain a *trans*-N–Sb–X system. If both these intramolecular N→Sb interactions per metal atom are considered [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],[19] the overall coordination becomes distorted square-pyramidal [$(C,N)_2SbE$ cores], with a carbon atom in the apical position, and the compounds can be described as hypervalent 12-Sb-5 species.[20,21]

The antimony–chalcogen distances in oxide **4** [Sb(1)–O(1) 1.986(3) Å] and sulfide **5** [Sb(1)–S(1) 2.4621(10) Å] are similar to the values found in the few related compounds described so far; for example, $(Ph_2Sb)_2O$ [1.978(3), 1.971(3) Å],[14] $(Me_2Sb)_2O$ [1.988(5), 2.099(6) Å],[12] and $(Me_2Sb)_2S$ [2.498(1) Å].[12]

The Sb(1)–E(1)–Sb(1a) angles in **4** [115.9(3)°] and **5** [100.78(5)°] are more acute than in $(Ph_2Sb)_2O$ [121.4(2)°],[14] $(Me_2Sb)_2O$ [123.0(3)°],[12] and $(Me_2Sb)_2S$ [92.35(5)°].[12] As observed for related $[\{2\text{-}(Me_2NCH_2)\text{-}C_6H_4\}_2Bi]_2E$ (E = O, S),[22] in these μ-chalcogeno species the bridging chalcogen atoms apparently behave as clips pressing together the two "soft" metal atoms. The torsion angles ϕ (ϕ = Sb–E–Sb-lp; E = O, S, and lp assumed position of the lone pair of electrons at Sb) are 8.2° in **4** and 10.2° in **5**, which is thus consistent with a *syn–syn*-conformation. A similar *syn–syn* conformation was observed for $(Ph_2Sb)_2O$[14] and $(Me_2Sb)_2S$,[12] whereas $(R_2Sb)_2O$ (R = Me,[12] *o*-tolyl, *p*-tolyl[14]) exhibit a *syn–anti* conformation.

The molecular structure of **6** comprises a $W(CO)_5$ moiety bound to the Sb atom of a diorganoantimony(III) hydroxide. Only one nitrogen atom is strongly coordinated to the antimony atom [Sb(1)–N(1) 2.860(9) Å], *trans* to the oxygen atom of the hydroxy group. The second pendant arm is twisted away from the metal center [nonbonding Sb(1)···N(2) distance of 3.739(8) Å] and its nitrogen atom is involved in an intramolecular hydrogen-bonding interaction with the H(1) atom of the hydroxy moiety [N(2)–H(1) 1.99(10) Å] (Figure 3). The antimony–oxygen bond length [Sb(1)–O(6) 1.976(7) Å] in **6** is similar to that observed in **5** and compares well with those observed in ionic organoantimony(V) species as the octahedral cation of $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_3SbOH]^+[I_3]^-$ [Sb–O 1.930(4) Å][9] or the tetrahedral cation of $[(2,6\text{-}Me_2C_6H_3)_3SbOH]^+[I]^-$ [Sb–O 1.907(2) Å].[23] The Sb(1)–W(1) bond length [2.7513(11) Å] is similar to those observed in other organoantimony(III) complexes containing $W(CO)_5$ groups; for example, $[(Ph_3Sb)W(CO)_5]$ [2.753(0) Å],[24] $[(Ph_2SbCH_2SbPh_2)\text{-}W(CO)_5]$ [2.743(1) Å], $[(Ph_2SbCH_2SbPh_2)\{W(CO)_5\}_2]$ [2.756(2) Å],[25] and $[(Ph_2SbCl)W(CO)_5]$ [2.7184(10) Å].[26] The resulting coordination geometry around antimony is distorted trigonal-bipyramidal (hypervalent 10-Sb-5 species), with O(6) and N(1) atoms in axial positions [N(1)–Sb(1)–O(6) 157.3(3)°] and C(1), C(10), and W(1) atoms in equatorial positions.

The five-membered SbC_3N rings formed through intramolecular coordination of the nitrogen atoms in compounds **3**–**5** are folded along the Sb···$C_{methylene}$ axis, with the nitrogen atom lying out of the best plane defined by the residual SbC_3 fragment. This folding induces planar chirality (with the aromatic ring and the nitrogen atom as chiral

plane and pilot atom, respectively; isomers given as S_N and R_N)[27] as described for other related main-group metal compounds.[9,10,22,28–33] Indeed, all compounds crystallize as racemates, that is, the crystal is composed of discrete (R_{N1},S_{N2}) and (S_{N1},R_{N2}) isomers for **3**, and (R_{N1},S_{N2}/R_{N1a},S_{N2a}) and (S_{N1},R_{N2}/S_{N1a},R_{N2a}) isomers for **4** and **5** (with respect to the two chelate rings at a metal center), respectively, with no unusual intermolecular distances shorter than the sum of the van der Waals radii between heavy atoms, or a heavy atom and H atoms.

For compound **6**, a second type of chirality is induced at the metal center in the trigonal-bipyramidal environment (isomers given as C_{Sb} and A_{Sb}).[34] Its crystal contains 1:1 mixtures of ($R_{N1}A_{Sb}$) and ($S_{N1}C_{Sb}$) isomers, which are associated into a polymeric chain build through weak intermolecular O(6)···H_{aryl} interactions [O(6)···H(4b) 2.57 Å; cf. Σr_{vdW}(O,H) ca. 2.60 Å[19]] (Figure 4). No interchain contacts are present.

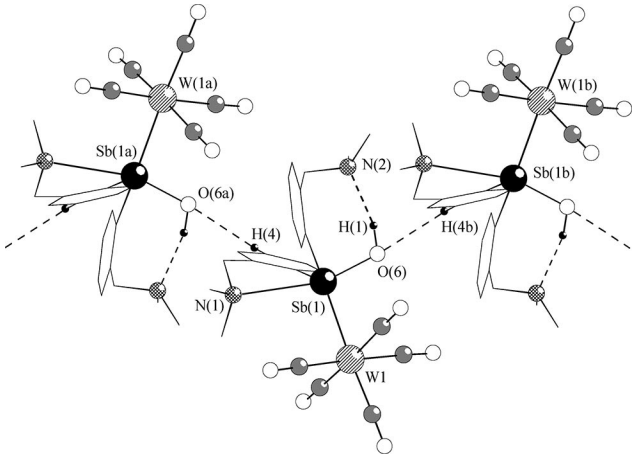
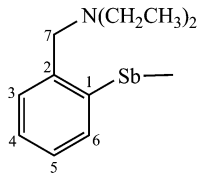


Figure 4. View along *c* axis of the chain polymer based on O···H contacts between alternating ($R_{N1}A_{Sb}$) and ($S_{N1}C_{Sb}$) isomers in the crystal of **6** (only hydrogen atoms involved in intermolecular interactions are shown) [symmetry equivalent atoms (–0.5 + *x*, 0.5 – *y*, –0.5 + *z*) and (0.5 + *x*, 0.5 – *y*, 0.5 + *z*) are denoted with an "a" and "b", respectively].

Solution Behavior

The ^{1}H and ^{13}C NMR resonances for compounds **3**–**6** were assigned on the basis of 2D experiments, according to the numbering pictured in Scheme 2.



Scheme 2.

The room-temperature ^{1}H NMR spectra of **3**–**6** exhibit only one set of resonances for the two 2-(Me_2NCH_2)C_6H_4 groups attached to the metal center. The ^{13}C NMR spectra of **4** and **5** also contain two singlet signals for the NMe_2 and CH_2 carbon atoms, as well as six singlet resonances in the aromatic region. These data suggest the equivalence of the aromatic groups bearing the pendant arms in a molecular unit on the NMR timescale. For all compounds the presence of a singlet ^{1}H resonance for the NMe_2 groups is consistent with fluxional behavior, which involves fast equilibrium between the strongly [N(1)] and the weakly [N(2)] bound pendant arms with nitrogen inversion. Similar behavior at room temperature was observed previously for the related [2-(Me_2NCH_2)C_6H_4]$_2$SbCl.[9] The AB spin system observed for the CH_2 groups in the ^{1}H NMR spectra of compounds **3**–**5** is consistent with a high configurational stability of the antimony atom at room temperature. By contrast, as for [2-(Me_2NCH_2)C_6H_4]$_2$SbCl,[9] the ^{1}H NMR spectrum of compound **6** exhibits a broad resonance for the methylene protons.

Conclusions

Usually, for organoantimony(III) derivatives such as $R_2SbCH_2SiMe_3$ (**3**) and $(R_2Sb)_2E$ [E = O (**4**), S (**5**)] [R = 2-(Me_2NCH_2)C_6H_4] that contain two organic groups with a pendant Me_2NCH_2 arm, both nitrogen atoms establish internal N→Sb interactions of different strengths in the solid state, which thus results in molecular species with distorted square-pyramidal $(C,N)_2SbE$ cores (hypervalent 12-Sb-5 species). Planar chirality is induced due to the folded five-membered SbC_3N rings, and the compounds crystallize as racemates. The NMR spectroscopic data for these compounds are consistent with configuration stability of the antimony atom. The reaction of oxide **4** with [$W(CO)_5$(thf)] results surprisingly in the isolation of the first hypervalent diorganoantimony(III) hydroxide metalcarbonyl complex [(R_2SbOH)$W(CO)_5$] (**6**). In this case, only one nitrogen atom is strongly coordinated to Sb, whereas the other nitrogen atom is involved in intramolecular hydrogen bonding with the hydroxy group. The coordination geometry around Sb is distorted trigonal bipyramidal (hypervalent 10-Sb-5 species), with a second type of chirality induced at the metal center.

Experimental Section

General Remarks: Room-temperature ^{1}H and ^{13}C NMR spectra were recorded with a Bruker DPX 200 instrument (^{1}H, 200 MHz; ^{13}C, 50 MHz) or with a Bruker AVANCE DRX 400 instrument (^{1}H, 400 MHz; ^{13}C, 100.6 MHz, including 2D experiments) by using solutions in dried solvents. The chemical shifts are reported in ppm relative to the residual peak of solvent (ref. $CHCl_3$: ^{1}H 7.26 ppm, ^{13}C 77.0 ppm; C_6D_6: ^{1}H 7.15 ppm, ^{13}C 128.02 ppm). Mass spectra were recorded with Finnigan MAT 8200 and MAT 95 instruments and IR spectra with an FTIR SPEKTRUM 1000. Elemental analyses were performed by Facultatea de Farmacie, Universitatea de Medicina si Farmacie "Iuliu Hatieganu", Cluj-Napoca (Romania). The manipulations were carried out under an inert atmosphere of argon (Linde, 99.999%) by using Schlenk techniques if not indicated otherwise. Solvents were dried and freshly

distilled under an atmosphere of argon prior to use. The compounds [2-(Me_2NCH_2)C_6H_4]$_2$SbCl [X = Cl (**1**), Br (**2**)][9] were prepared according to published methods. Other starting materials such as Me_3SiCH_2Cl, Mg turnings, $Na_2S{\cdot}xH_2O$, elemental sulfur, and $W(CO)_6$ were commercially available.

[2-(Me_2NCH_2)C_6H_4]$_2$SbCH$_2$SiMe$_3$ (3): A solution of Me_3SiCH_2Cl (0.84 g, 6.85 mmol) in thf (100 mL) was added dropwise to Mg turnings (0.2 g, 8.16 mmol) activated with 1,2-dibromoethane (0.7 mL). The reaction mixture was stirred for 12 h and then filtered and added dropwise to a solution of [2-(Me_2NCH_2)C_6H_4]$_2$SbCl (**1**; 2.89 g, 6.79 mmol) in thf (50 mL). The reaction mixture was stirred for another 12 h, and the solvent was then removed under vacuum. After extraction with hexane (150 mL) and filtration, the clear solution was concentrated and cooled to –28 °C to give **3** (1.3 g, 40%) as colorless crystals. M.p. 75–77 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.02 (s, 9 H, Si-CH_3), 0.64 (s, 2 H, -CH_2-Si), 2.01 (s, 12 H, N-CH_3), AB spin system with δ_A = 3.34 and δ_B = 3.52 ($^2J_{H,H}$ = 12.6 Hz, 4 H, -CH_2-N), 7.15 (m, 6 H, 3,4,5-H, -C_6H_4-), 7.47 (m, 2 H, 6-H, -C_6H_4-) ppm. MS (EI, 70 eV): *m*/*z* (%) = 475 (5) [M$^+$], 461 (8) [M$^+$ – CH_3], 389 (100) [($Me_2NCH_2C_6H_4$)$_2$Sb$^+$], 134 (42) [$Me_2NCH_2C_6H_4^+$]. $C_{22}H_{35}N_2SbSi$ (477.36): calcd. C 55.35, H 7.39, N 5.87; found C 54.98, H 7.43, N 5.57.

[{2-(Me_2NCH_2)C_6H_4}$_2$Sb]$_2$O (4): A solution of [2-(Me_2NCH_2)-C_6H_4]$_2$SbBr (**2**; 2.54 g, 5.40 mmol) in thf (70 mL) was added dropwise, whilst stirring, to Mg turnings (0.13 g, 5.42 mmol) activated with 1,2-dibromoethane (1 mL). The reaction mixture was stirred for 12 h, and the solvent was then removed under vacuum. The remaining solid product was treated with toluene (150 mL), the insoluble material was filtered by suction under an atmosphere of argon, and oxygen was bubbled for 1 h through the clear orange solution. The solution turned colorless, and removal of the solvent under vacuum gave **4** (1.8 g, 84%) as a white solid. M.p. 151–153 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.00 (s, 24 H, N-CH_3), AB spin system with δ_A = 3.22 and δ_B = 3.37 ($^2J_{H,H}$ = 13.1 Hz, 4 H, -CH_2-N), 7.04 (d, $^3J_{H,H}$ = 6.3 Hz, 4 H, 3-H, -C_6H_4-), 7.19 (m, 8 H, 4,5-H, -C_6H_4-), 7.77 (d, $^3J_{H,H}$ = 6.9 Hz, 4 H, 6-H, -C_6H_4-) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 44.56 (s, N-*C*H$_3$), 65.36 (s, -*C*H$_2$-N), 127.45, 128.19 (s, C-3,4,5), 135.31 (s, C-6), 143.63 (s, C-2), 148.71 (s, C-1) ppm. MS (EI, 70 eV): *m*/*z* (%) = 796 (8) [M$^+$], 662 (15) [M$^+$ – R], 405 (5) [($Me_2NCH_2C_6H_4$)$_2$SbO$^+$], 389 (100) [($Me_2NCH_2C_6H_4$)$_2$Sb$^+$], 134 (63) [$Me_2NCH_2C_6H_4^+$]. $C_{36}H_{48}N_4OSb_2$ (796.28): calcd. C 54.30, H 6.08, N 7.04; found C 54.65, H 6.39, N 7.32.

[{2-(Me_2NCH_2)C_6H_4}$_2$Sb]$_2$S (5)

Procedure 1: A solution of $Na_2S{\cdot}9H_2O$ (0.72 g, 3.00 mmol) in water (40 mL) was added to a solution of [2-(Me_2NCH_2)C_6H_4]$_2$SbCl (**1**; 2 g, 4.70 mmol) in toluene (60 mL). The mixture was stirred for 12 h at room temperature. The yellow organic phase was then separated, and the water phase was washed with toluene (2 × 30 mL). The toluene solution was dried with anhydrous Na_2SO_4. Removal of the solvent under vacuum gave **5** (1.6 g, 84%) as a yellow solid.

Procedure 2: A solution of [2-(Me_2NCH_2)C_6H_4]$_2$SbBr (**2**; 2.49 g, 5.30 mmol) in thf (70 mL) was added dropwise, whilst stirring, to Mg turnings (0.13 g, 5.42 mmol) activated with 1,2-dibromoethane (1 mL). The reaction mixture was stirred for 12 h, and the solvent was then removed under vacuum. The remaining solid product was treated with toluene (150 mL), the insoluble material filtered off by suction, and sulfur (0.086 g, 2.69 mmol) was added to the clear orange solution. The reaction mixture was stirred for 3 h and then filtered, and the solvent was removed under vacuum to give **5** (1.7 g, 79%) as a yellow solid. M.p. 191–194 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.06 (s, 24 H, N-CH_3), AB spin system with δ_A = 3.42 and δ_B = 3.57 ($^2J_{H,H}$ = 13.2 Hz, 4 H, -CH_2-N), 7.14 (m, 12 H, 3,4,5-H, -C_6H_4-), 7.92 (m, 4 H, 6-H, -C_6H_4-) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 44.08 (s, N-*C*H$_3$), 65.89 (s, -*C*H$_2$-N), 127.26, 127.52, 127.60 (s, C-3,4,5), 136.99 (s, C-6), 143.26 (s,

Table 2. Crystallographic data for compounds **3**–**6**.

	3	**4**	**5**	**6**
Empirical formula	$C_{22}H_{35}N_2SbSi$	$C_{36}H_{48}N_4OSb_2$	$C_{36}H_{48}N_4SSb_2$	$C_{23}H_{25}N_2O_6SbW$
M	477.36	796.28	812.34	731.05
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$	$C2/c$	$P2_1/n$
a [Å]	9.325(4)	12.696(3)	27.561(6)	10.787(4)
b [Å]	14.391(6)	14.474(3)	7.4266(15)	19.076(7)
c [Å]	18.193(7)	19.948(4)	18.748(4)	12.598(5)
α [°]	90	90	90	90
β [°]	95.642(8)	98.542(4)	112.22(3)	93.03
γ [°]	90	90	90	90
V [Å^3]	2429.4(17)	3625.1(14)	3552.4(12)	2588.7(17)
Z	4	4	4	4
$D_{calcd.}$ [g cm^{-3}]	1.305	1.459	1.519	1.876
F(000)	984	1608	1640	1400
Crystal size [mm]	0.22 × 0.11 × 0.09	0.43 × 0.23 × 0.18	0.50 × 0.35 × 0.10	0.50 × 0.30 × 0.30
μ(Mo-K_α) [mm^{-1}]	1.193	1.522	1.610	5.522
θ range [°]	1.81–26.38	2.06–25.00	2.35–25.00	2.17–25.00
Completeness to 2θ	0.999	1.000	0.999	0.998
No. of reflections collected	19247	17043	17126	5772
No. of independent reflections	4975 (R_{int} = 0.0562)	3207 (R_{int} = 0.0442)	3121 (R_{int} = 0.0658)	4541 (R_{int} = 0.0382)
No. of parameters	242	199	199	309
Absorption correction	Multi-Scan[37]	Multi-Scan[37]	Refdelf[38]	Refdelf[38]
R_1 [$I > 2\sigma(I)$]	0.0434	0.0492	0.0266	0.0476
wR_2	0.0815	0.1014	0.0621	0.0908
GOF on F^2	1.069	1.221	0.941	0.987
Largest diff. electron density [e Å^{-3}]	0.478/–0.581	0.820/–1.490	0.766/–0.316	1.220/–1.031

C-2), 145.24 (s, C-1) ppm. MS (EI, 70 eV): *m/z* (%) = 812 (10) [M^+], 678 (6) [M^+ – R], 421 (11) [$(Me_2NCH_2C_6H_4)_2SbS^+$], 389 (100) [$(Me_2NCH_2C_6H_4)_2Sb^+$], 134 (35) [$Me_2NCH_2C_6H_4^+$]. $C_{36}H_{48}N_4SSb_2$ (812.34): calcd. C 53.23, H 5.96, N 6.90; found C 53.02, H 6.12, N 6.62.

[({2-(Me_2NCH_2)C_6H_4}$_2$SbOH)W(CO)$_5$] (6): A mixture of [{2-(Me_2NCH_2)C_6H_4}$_2$Sb]$_2$O (**4**; 1.24 g, 1.60 mmol) and $W(CO)_5$(thf) [prepared from $W(CO)_6$ (1.20 g, 3.41 mmol) by irradiation with an UV lamp] in thf (130 mL) was stirred for 12 h at room temperature. The solvent was removed under vacuum, and the remaining yellow-orange product was washed with petroleum ether (2 × 100 mL) and toluene (100 mL). Compound **6** (1.2 g, 51%) was obtained as orange crystals by cooling the concentrated solution at –28 °C. M.p. 130 °C. IR (nujol): $\tilde{\nu}$ = 2068 (s), 1964 (s), 1948 (s), 1913 [s (C=O)] cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ = 1.84 (br. s, 12 H, N-C*H*$_3$), 3.27 (br. s, 4 H, -C*H*$_2$-N), 6.80 (br. s, 1 H, O*H*), 7.40 (m, 8 H, 3,4,5-H, -C_6H_4-), 8.11 (br. s, 2 H, 6-H, -C_6H_4-) ppm. MS (EI, 70 eV): *m/z* (%) = 730 (14) [M^+], 702 (6) [M^+ – CO], 674 (5) [M^+ – 2CO], 646 (5) [M^+ – 3CO], 618 (7) [M^+ – 4CO], 590 (4) [M^+ – 5CO], 389 (100) [$(Me_2NCH_2C_6H_4)_2Sb^+$], 134 (73) [$Me_2NCH_2C_6H_4^+$]. MS (ESI+, thf/CH_3CN): *m/z* (%) = 405 (25) [M^+ –$W(CO)_5$], 389 (100) [$(Me_2NCH_2C_6H_4)_2Sb^+$], 134 (16) [$Me_2NCH_2C_6H_4^+$]. $C_{23}H_{25}N_2O_6SbW$ (731.05): calcd. C 37.79, H 3.45; found C 37.46, H 3.09.

X-ray Crystallographic Study: The details of the crystal structure determination and refinement for compounds **3**–**6** are given in Table 2. Data were collected with Bruker SMART APEX (**3**, **4**), Stoe IPDS (**5**), and Siemens P4 (**6**) diffractometers by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). For this purpose, the crystals were attached on cryoloops (**3**, **4**) or with Kel-F oil (**5**, **6**) to a glass fiber. Data for **3** and **4** were collected at room temperature (297 K), whereas for **5** and **6** the crystals were cooled under a nitrogen stream at low temperature. The structures were refined with anisotropic thermal parameters. The hydrogen atom attached to the oxygen atom in **6** was located from the difference map. The other 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.[35] The drawings were created with the Diamond program.[36] CCDC-709978 (for **3**), -709979 (for **4**), -709980 (for **5**), and -709981 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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