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Triethylantimony(V) complexes with bidentate *O,N*-, *O,O*- and tridentate *O,N,O′*-coordinating *o*-iminoquinonato/*o*-quinonato ligands: Synthesis, structure and some properties

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ABSTRACT

The novel triethylantimony(v) *o*-amidophenolato (AP-R)$SbEt_3$ (R = *i*-Pr, **1**; R = Me, **2**) and catecholato (3,6-DBCat)$SbEt_3$ (**3**) complexes have been synthesized and characterized by IR, NMR spectroscopy (AP-R is 4,6-di-*tert*-butyl-*N*-(2,6-dialkylphenyl)-*o*-amidophenolate, alkyl = isopropyl (**1**) or methyl (**2**); 3,6-DBCat is 3,6-di-*tert*-butyl-catecholate). Complexes **1**–**3** have been obtained by the oxidative addition of corresponding *o*-iminobenzoquinones or *o*-benzoquinones to Et_3Sb. The addition of 4,6-di-*tert*-butyl-*N*-(3,5-di-*tert*-butyl-2-hydroxyphenyl)-*o*-iminobenzoquinone to Et_3Sb at low temperature gives hexacoordinate [(AP-AP)H]$SbEt_3$ (**4**) which decomposes slowly in vacuum with the liberation of ethane yielding pentacoordinate complex [(AP-AP)]$SbEt_2$ (**5**). $[(AP\text{-}AP)H]^{2-}$ is O,N,O′-tridentate amino-bis-(3,5-di-*tert*-butyl-phenolate-2-yl) dianion and $[(AP\text{-}AP)]^{3-}$ is amido-bis-(3,5-di-*tert*-butyl-phenolate-2-yl) trianion. The decomposition of **4**–**5** accelerates in the presence of air. *o*-Amidophenolates **1** and **2** bind molecular oxygen to give spiroendoperoxides $Et_3Sb[L\text{-}iPr]O_2$ (**6**) or $Et_3Sb[L\text{-}Me]O_2$ (**7**) containing trioxastibolane rings. This reaction proceeds slowly and reaches the equilibrium at 15–20% conversion five times more than for (AP-R)$SbPh_3$ analogues. Molecular structures of **1** and **5** were determined by X-ray analysis.

1. Introduction

The coordination chemistry of redox-active *o*-benzoquinonato and *o*-iminobenzoquinonato ligands attracts the scientist's attention during 30 years at the least. Unusual and interesting phenomena have been observed on *o*-quinonato/*o*-iminoquinonato complexes. Among them are "photo/thermomechanical effect" [1–3], valence tautomerism [4–13], "wandering valence", elementotropy [14] etc. Transition metal *o*-semiquinonato/*o*-iminosemiquinonato (SQ/ISQ) complexes demonstrate a versatility of structural types, different types of magnetic exchange depending on complex structure as well as the nature of central atom and ligands [7,15–20], etc. Non-transition metal complexes also reveal interesting magnetic properties depending on metal nature and complex geometry [21–25], they can serve as model objects for the investigation of ligand-to-ligand magnetic exchange [21–25], as the spin traps [26–28]. Four years earlier, we have found that complexes of non-transition metals with redox-active ligands are able to demonstrate chemical behavior typical for transition metal complexes. We have found that triphenylantimony(V) *o*-amidophenolato complexes, (AP)$SbPh_3$, where *o*-amidophenolato is dianion of *o*-iminobenzoquinone, and some catecholates (Cat)$SbPh_3$, can bind molecular oxygen in a reversible manner [29–31]. This unique ability is caused by the combination of redox-active dianionic AP/Cat ligand (which is oxidized by molecular oxygen to radical-anion) and heavy antimony atom, which has a large spin–orbit constant (this feature of antimony facilitates an inter-spin conversion) and a vacant site to coordinate superoxide radical-anion (Scheme 1) according to the proposed mechanism [29,31].

The complex ability to bind dioxygen depends on the redox-potential of AP or Cat ligand. We have shown that a number of triphenylantimony(V) catecholates with an acceptor substituents (such as Cl, Br, F, NO_2) at Cat ligand are inactive in reaction with dioxygen [32,33] while donor groups (for example, methoxy-groups) in Cat ligand allow the complex derived to be dioxygen-active [30,31]. On the other hand, the tridentate O,N,O′-ligand *o*-iminobenzoquinone with hydroxyl-group at N-aryl forms amino-bis-phenolate triphenylantimony(V) complex which is air-stable due to its structural features: it cannot form stable *o*-iminobenzosemiquinonato radical-anion upon oxidation [34]. What about chemical properties of Cat and AP complexes of antimony(V) with ethyl groups instead of phenyls? In this paper, we report the synthesis of new *o*-amidophenolato triethylantimony(V) complexes with bidentate O,N- and

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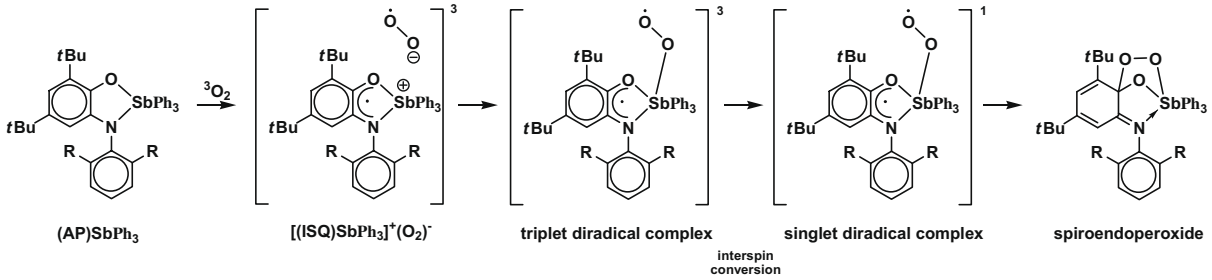


Scheme 1.

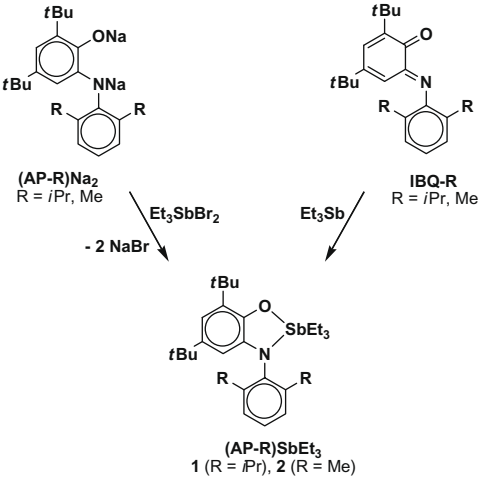
tridentate O,N,O′-ligands, its 3,6-di-*tert*-butyl-catecholate analogue, and the investigation of the dioxygen activity of complexes.

2. Results and discussion

o-Amidophenolato triethylantimony(V) complexes may be prepared by two different methods (Scheme 2). The first is a classic exchange reaction of *o*-amidophenolato alkali salts (AP-R)M_2 (M = Na, K) with Et_3SbBr_2 [18,35]. The second way is an oxidative addition of neutral *o*-iminobenzoquinones (IBQ-R) to low-valent antimony compounds. Noteworthy, the reaction of Et_3Sb with *o*-iminobenzoquinones proceeds as the two-electron oxidation but not as the 1,2- or 1,4-nucleophylic addition usual for reactions of *o*-quinones with dialkyl alkali-earth metals (Et_2Zn, Et_2Cd, etc.) [36]. The yield of (AP-R)$SbEt_3$ (R = *i*Pr, **1**; R = Me, **2**) in reaction is close to quantitative (~98%).

Complexes **1** and **2** were isolated as bright-yellow crystalline powders stable in solutions as well as in solid under oxygen-free conditions. Compounds were characterized by ^1H, ^{13}C NMR, IR spectroscopy. The crystal structure of (AP-*i*Pr)$SbEt_3$ (**1**) was determined using single-crystal X-ray studies. The spectral characteristics of complexes prepared by different method are identical.

The NMR spectroscopy of **1** and **2** shows that alkyl groups at 2 and 6 positions of N-aryl fragment are equal. For instance, methyne protons in **1** appears in ^1H NMR spectrum as one septet at 3.16 ppm with spin-spin coupling constant $^4J_{HH}$ = 6.86 Hz and methyl protons of isopropyls give two doublets at 1.03 and 1.18 ppm ($^3J_{HH}$ = 6.9 Hz). Ethyl groups of $SbEt_3$ moiety are nearly equal in NMR time scale: they give rise to two quartets (1:2) with nearly identical chemical shift at $\delta \approx 1.61$ ppm with $\Delta\delta < 0.005$ ppm from six methylene protons, and triplet at 1.29 ppm from nine methyl protons ($^3J_{HH}$ = 7.5 Hz). It is interesting



Scheme 2.

that the samples of complexes **1** and **2** prepared by the first method demanding the coordinating solvent (THF) do not contain THF as the ligand on central antimony atom.

The crystal structure of **1** was determined by X-ray analysis and a PLATON diagram is shown in Fig. 1; selected bond distances and angles are collected in Table 1.

Compound **1** has a slightly distorted trigonal bipyramidal environment at Sb(1) with the base formed by N(1), C(27) and C(29) atoms (the bond angle sum is 356.2(3)°). The apical positions are occupied by oxygen atom O(1) and carbon atom C(31); the angle C(31)–Sb(1)–O(1) is 169.81(7)°. The chelate ring is almost planar: the torsion angle O(1)–C(1)–C(2)–N(1) is 0.82(6)°, and the bent angle along O(1)···N(1) line is 0.4°. The geometrical characteristics of AP ligand are completely consistent with its dianionic nature [18], O(1)–C(1) and N(1)–C(2) bonds of 1.350(2) and 1.396(3) Å are close to the corresponding bonds in triphenylantimony(V) analogue (AP-*i*Pr)$SbPh_3$ (1.351(4) and 1.408(4) Å, correspondingly) [29]. The average carbon-carbon bond length in six-membered ring of AP ligand (1.395 ± 0.014 Å) is indicative of its aromaticity. The plane of this ring C(1–6) is nearly orthogonal to the plane of N-aryl group with the angle of 86.92°. The unit cell of **1** contains two enantiomers of complex with different rotating sense of three ethyl groups. Noteworthy is that antimony(V)-heteroatom bond lengths in **1** and its triphenylantimony(V) analogue (AP-*i*Pr)$SbPh_3$ are sufficiently close: the O(1)–C(1) and N(1)–C(2) bonds are 2.0843(15) and 2.0418(16) Å in **1** while in (AP-*i*Pr)$SbPh_3$ they are 2.074(2)

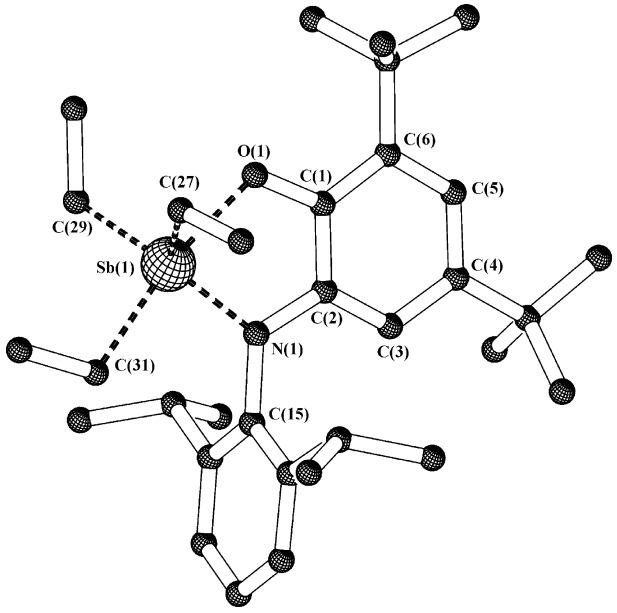


Fig. 1. X-ray structure of (AP-*i*Pr)$SbEt_3$ (**1**) (PLATON presentation [37]). Hydrogen atoms are omitted for clarity.

Table 1
Selected bond distances (Å) and bond angles (°) in **1**.

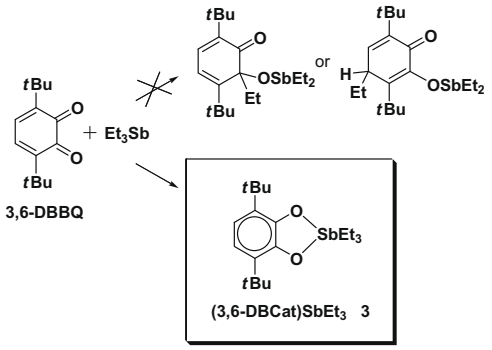
Bond (Å)		Angle (°)	
Sb(1)–N(1)	2.0418(16)	N(1)Sb(1)O(1)	77.40(6)
Sb(1)–O(1)	2.0843(15)	N(1)Sb(1)C(27)	125.66(13)
Sb(1)–C(27)	2.129(3)	O(1)Sb(1)C(27)	85.13(11)
Sb(1)–C(29)	2.142(3)	N(1)Sb(1)C(29)	119.12(10)
Sb(1)–C(31)	2.161(2)	O(1)Sb(1)C(29)	88.91(9)
O(1)–C(1)	1.350(2)	C(27)Sb(1)C(29)	111.40(14)
N(1)–C(2)	1.396(3)	N(1)Sb(1)C(31)	92.73(8)
N(1)–C(15)	1.439(3)	O(1)Sb(1)C(31)	169.81(7)
C(29)–C(30)	1.487(4)	C(27)Sb(1)C(31)	98.91(12)
C(27)–C(28)	1.354(5)	C(29)Sb(1)C(31)	98.21(11)
C(31)–C(32)	1.509(3)	C(2)N(1)C(15)	120.00(16)
C(1)–C(2)	1.409(3)	C(2)N(1)Sb(1)	116.20(12)
C(2)–C(3)	1.385(3)	C(15)N(1)Sb(1)	123.79(14)
C(3)–C(4)	1.392(3)	C(30)C(29)Sb(1)	115.1(2)
C(4)–C(5)	1.390(3)	C(28)C(27)Sb(1)	117.1(3)
C(5)–C(6)	1.401(3)	C(32)C(31)Sb(1)	112.14(17)
C(6)–C(1)	1.390(3)		

and 2.041(3) Å, correspondingly. This observation indicates a negligible dependence of these distances on the nature of alkyl/aryl substituents at Sb(V) atom.

As mentioned above, zinc and cadmium alkyl organometallics (Et_2Zn, Et_2Cd, etc.) react with 3,6-di-*tert*-butyl-*o*-benzoquinone through the 1,2- or 1,4-nucleophylic addition mechanism [36]. We have treated triethylstibine with one equivalent of 3,6-DBBQ (Scheme 3). Surprisingly, in this case the single product of reaction was triethylantimony(V) catecholate (3,6-DBCat)$SbEt_3$ (**3**) but not 3,6-di-*tert*-butyl-2-(diethylstibinooxy)-2-ethylcyclohexa-3,5-dienone or 3,6-di-*tert*-butyl-2-(diethylstibino-oxy)-4-ethylcyclohexa-2,5-dienone – the possible products of 1,2- and 1,4-nucleophilic addition [36].

Catecholate **3** was isolated with the yield of 95%; it is a pale yellow crystalline solid which is easily soluble in different non-polar solvents such as pentane, hexane, benzene, toluene and even more in diethyl ether, THF etc. Complex may be stored for a long time in solid state under air-free conditions.

The third common way to *o*-quinonato and *o*-iminobenzoquinonato complexes is an exchange reaction of metal salts with the corresponding catechol or *o*-aminophenol in the presence of base [18,35]. This method being applied to Et_3SbBr_2 gave the hexacoordinate compound [(AP-AP)H]$SbEt_3$ (**4**) with O,N,O′-tridentate amino-bis-phenolate ligand $[(AP\text{-}AP)H]^{2-}$ (Scheme 4). This complex was isolated as nearly colorless microcrystalline solid which should be stored in vacuo under low temperature because of its quite easy decomposition at room temperature and on air (see below). The structures of compounds **3** and **4** were determined by ^1H, ^{13}C and IR spectroscopy. Compound **4** is related to triphenylantimony(V) complex [(AP-AP)H]$SbPh_3$ [34]. Both complexes have a symmetry plane dividing complex to two symmetrical parts. However, chemical behavior of complexes is rather different. If triphenylantimony complex [(AP-AP)H]$SbPh_3$ is stable on the exposition to air, and it does not undergo any decomposition at ambient temperature, its triethylantimony analogue **4** decomposes slowly in vacuo with the liberation of ethane yielding pentacoordinate complex [(AP-AP)]$SbEt_2$ (**5**) (Scheme 4). Fig. 2 shows the changes in ^1H NMR spectrum upon transformation of **4** to **5**. Worthy of note is the symmetry plane of molecule remains in **5** like as in **4** that is clearly obvious from the NMR spectrum. NMR spectroscopy shows the disappearance of amino proton signal (singlet at $\delta = 4.96$ ppm) in **5**, and this fact is corroborated by the absence of stretch vibration band of NH-group in IR spectrum of **5**.



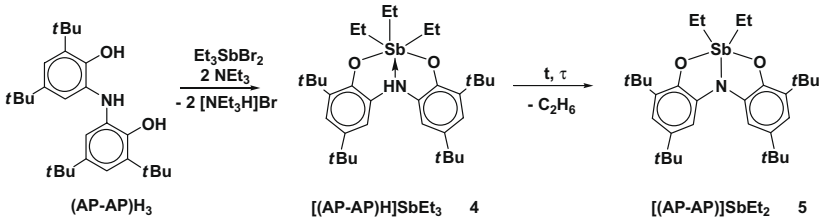
Scheme 3.

The decomposition accelerates in the presence of oxygen. However in this case, in the addition to complex **5**, we have found among decomposition products diethyl ether and ethanol using NMR spectroscopy. Apparently, they are formed from ethyl groups of $SbEt_3$ fragment. Complex **5** was found to be air-stable; it was isolated as X-ray suitable pale yellow crystals (Fig. 3).

The antimony atom Sb(1) possesses trigonal bipyramidal geometry where the byramid base is formed by atoms N(1), C(29) and C(31) (the angle sum is 360.0(1)°), The bond angle between apical oxygen substituents O(1)–Sb(1)–O(2) is 159.30(4)° reflecting the bipyramid distortion. Both six-membered carbon rings have aromatic character with average C-C distance of 1.396 ± 0.012 Å that is very close to value for *o*-amidophenolate **1**. The O(1)–C(1) and O(2)–C(7) as well as N(1)–C(2) and N(1)–C(8) bonds are equal within the experimental error (see Table 2). They are close to values of single O-C and O-N bonds in complexes of O,N-bidentate *o*-amidophenolato ligands [18,29] and, at the same time, remarkably longer than those bonds in transition metal complexes with O,N,O′-ligand in oxidation levels −1, −2 (for example, O–C, 1.267(5) Å, N–C, 1.344(5) Å in $Ni^{II}(AP\text{-}IBQ)_2$ [38]; O–C, 1.297(3) Å, N–C, 1.357(3) Å in $Fe^{III}(AP\text{-}ISQ)(AP\text{-}IBQ)$ [39]; O–C, av. 1.305(7) Å, N–C, av. 1.362(6) Å in $Co^{III}(AP\text{-}ISQ)(AP\text{-}IBQ)$ [40]; O–C, av. 1.326(7) Å, N–C, av. 1.379(7) Å in $V^{IV}(AP\text{-}ISQ)_2$ [41], O–C, av. 1.325(9) Å, N–C, av. 1.381(9) Å in $Mn^{IV}(AP\text{-}ISQ)_2$ [40], where AP-IBQ is monoanion, AP-ISQ is dianion-radical). The nitrogen atom N(1) is planar and sp^2-hybridized pointing to its amido-nature. So, the geometric characteristics of this O,N,O′-bis-chelate ligand reflect its clear trianionic nature. Noteworthy, $[(AP\text{-}AP)]^{3-}$ ligand in **5** is not planar (Fig. 4). The angle between the planes of phenyl rings is 25.8(1)° being significantly larger than those angles in transition metal complexes with this type O,N,O′-ligand (what about transition metal complexes, the highest value of this twist angle is 13.4° for $Mn^{IV}(AP\text{-}ISQ)_2$ complex [40], in other complexes it is 5–12°). The deviation of the phenyl rings in O,N,O′-ligand from coplanarity can be attributed to the sterical repulsion between *tert*-butyl substituents of rings; the same situation is described for tin complex $Sn^{IV}(AP\text{-}ISQ)_2$ (the corresponding angles are 30.4(7)° and 28.7(7)° for two ligands, [42]).

Triethylantimony(V) complex **4** was also prepared by the oxidative addition of 4,6-di-*tert*-butyl-*N*-(3,5-di-*tert*-butyl-2-hydroxyphenyl)-*o*-iminobenzoquinone **(IBQ-AP)H** to triethylstibine (Scheme 5). Remarkably, the reagent addition order determines the final reaction product. Complex **4** is formed when the ligand (IBQ-AP)H is added dropwise to a solution of triethylstibine. If the order is inversed, the main product is diethylantimony(V) derivative **5**. Apparently, in the second case complex **4** formed is attacked by the neutral (IBQ-AP)H ligand which plays role of dehydrogenating agent yielding complex **5**.

In previous papers we have reported the reversible binding of molecular oxygen by triphenylantimony(V) *o*-amidophenolates with the formation of spiroendoperoxide species [29–31]. The change of phenyl groups with ethyl substituents at antimony (complexes **1**, **2**) results in a change of complexes reactivity: *o*-amidophenolates **1** and **2** react with molecular oxygen (Scheme 6) to



Scheme 4.

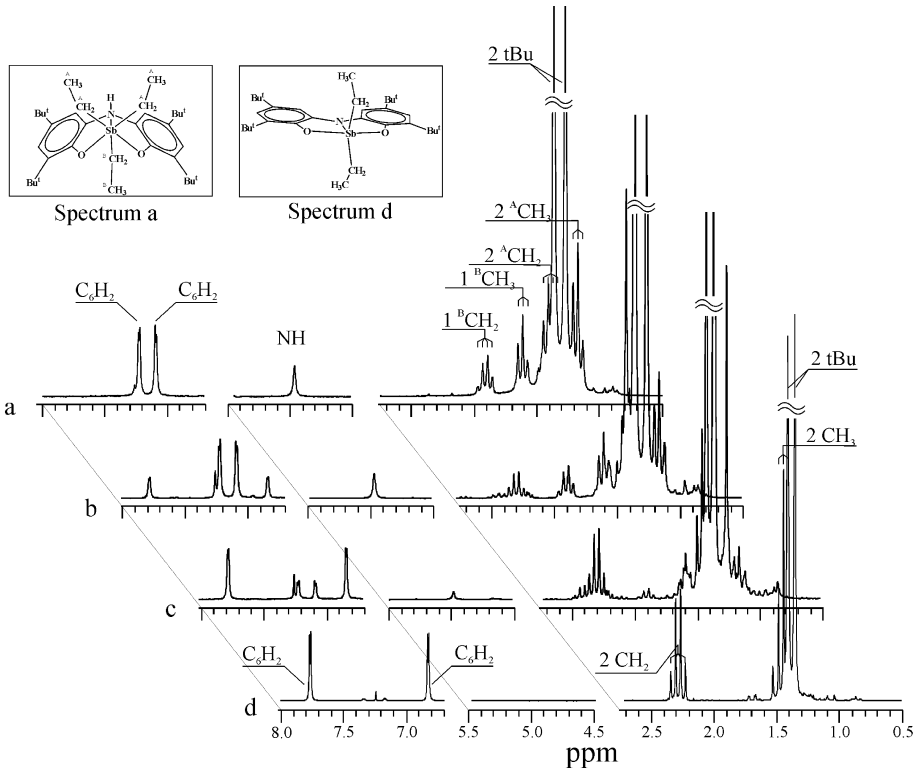


Fig. 2. ^{1}H NMR spectra: (a) clear [(AP-AP)H]SbEt$_3$ (**4**), (b, c) the reaction mixtures during the conversion of **4** to **5**; and (d) resulting [(AP-AP)]SbEt$_2$ (**5**) (conditions: CDCl$_3$, 298 K).

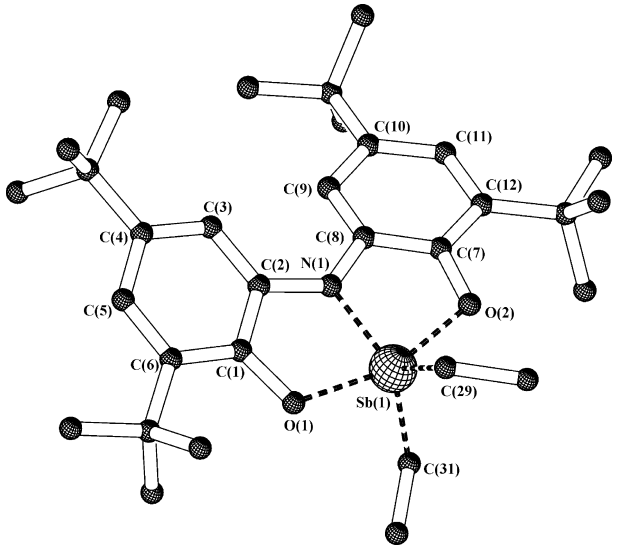


Fig. 3. X-ray structure of [(AP-AP)]SbEt$_2$ (**5**). The H atoms are omitted for clarity.

Table 2
Selected bond distances (Å) and bond angles (°) in **5**.

Bond (Å)		Angle (°)	
Sb(1)–O(1)	2.0338(10)	O(1)Sb(1)O(2)	159.29(4)
Sb(1)–O(2)	2.0310(10)	N(1)Sb(1)O(1)	79.61(4)
Sb(1)–N(1)	2.0011(12)	N(1)Sb(1)O(2)	79.69(5)
Sb(1)–C(31)	2.1157(16)	N(1)Sb(1)C(31)	121.90(6)
Sb(1)–C(29)	2.1173(16)	N(1)Sb(1)C(29)	122.01(6)
O(1)–C(1)	1.3633(17)	O(1)Sb(1)C(31)	93.26(6)
O(2)–C(7)	1.3644(17)	O(1)Sb(1)C(29)	96.81(6)
N(1)–C(2)	1.3992(18)	O(2)Sb(1)C(31)	97.62(5)
N(1)–C(8)	1.3994(18)	O(2)Sb(1)C(29)	94.15(6)
C(1)–C(2)	1.4075(18)	C(31)Sb(1)C(29)	116.08(7)
C(1)–C(6)	1.4019(19)	C(1)O(1)Sb(1)	113.51(8)
C(2)–C(3)	1.3865(19)	C(7)O(2)Sb(1)	113.49(8)
C(3)–C(4)	1.3897(19)	C(2)N(1)C(8)	130.30(12)
C(4)–C(5)	1.3947(19)	C(2)N(1)Sb(1)	115.00(9)
C(5)–C(6)	1.3948(19)	C(8)N(1)Sb(1)	114.69(9)
C(7)–C(8)	1.4085(19)	C(30)C(29)Sb(1)	113.61(12)
C(7)–C(12)	1.3972(19)	C(32)C(31)Sb(1)	112.21(11)
C(8)–C(9)	1.3890(20)		
C(9)–C(10)	1.3859(19)		
C(10)–C(11)	1.3960(20)		
C(11)–C(12)	1.3980(20)		

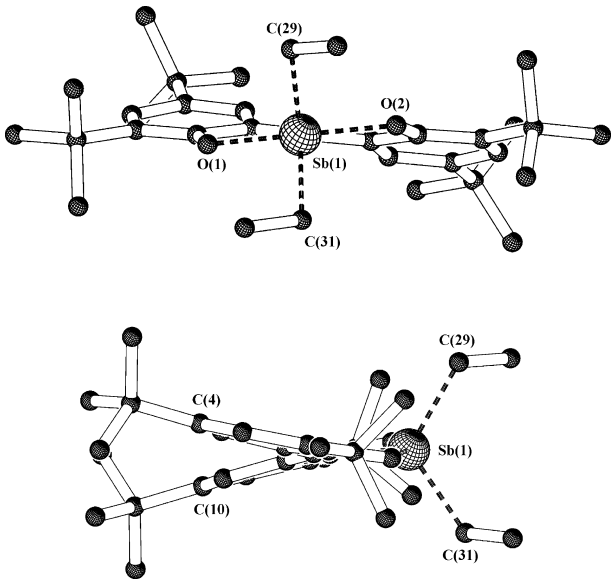
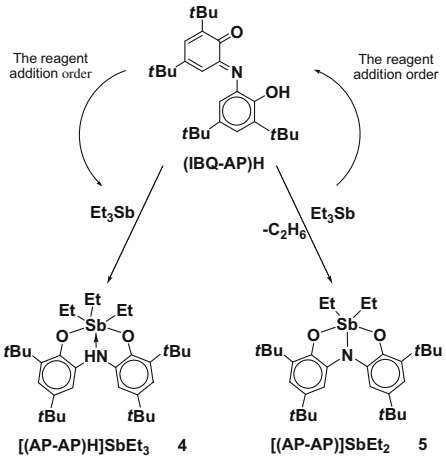
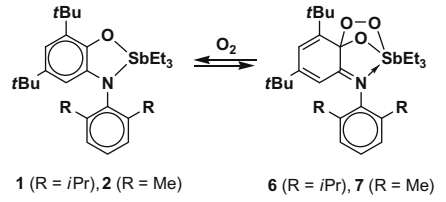


Fig. 4. Views on complex **5** molecule. Hydrogen atoms are omitted for clarity.



Scheme 5.



Scheme 6.

give spiroendoperoxides **6** and **7**, correspondingly, slower than their triphenylantimony analogues. The reaction reaches an equilibrium five times slower than for (AP-R)$SbPh_3$ and amounts to 15–20% of conversion compared with 94–98% conversion of (AP-R)$SbPh_3$.

The removal of oxygen leads to the shift of this equilibrium with the formation of initial *o*-amidophenolates **1**, **2**. At the same time, the prolonged exposition of these complexes to air allows deeper subsequent oxidation of spiroendoperoxides **6** and **7**.

The decrease of *o*-amidophenolates conversion to spiroendoperoxides can be rationalized from the viewpoint of the mechanism proposed [29,31]. The first stage (one-electron oxidation of dianionic AP ligand to radical-anion by molecular oxygen) is followed by the coordination of superoxide anion to antimony(V) to form a triplet diradical complex containing *o*-iminobenzosemiquinonato and end-on bound peroxo-ligands. The initial coordination of molecular oxygen to antimony (which should forego the first stage) depends on the sensitivity to the electrophylic attack. The latter can be controlled by the positive charge on antimony which decreases in Et_3Sb compared with Ph_3Sb. In the former case, ethyl groups donate the electronic density to antimony decreasing its positive charge, and it makes dioxygen-binding ability to be less pronounced.

3. Experimental

3.1. General considerations

All manipulations were carried out under an air-free atmosphere. All solvents were purified using standard technique [43]. Diethyl ether was distilled from sodium benzophenone ketyl and degassed immediately prior to use. Hexane and toluene were distilled from CaH_2 and degassed immediately prior to use. Deuterated chloroform was dried with phosphorus(V) oxide and vacuum-transferred. Anhydrous $SbCl_3$, $SbPh_3$ and EtBr were purchased. Et_3SbBr_2 and Et_3Sb [44,45], 4,6-di-*tert*-butyl-*N*-(2,6-di-isopropylphenyl)-*o*-iminobenzoquinone **IBQ-iPr**, 4,6-di-*tert*-butyl-*N*-(2,6-dimethylphenyl)-*o*-iminobenzoquinone **IBQ-Me** [46].

The synthesis of 4,6-di-*tert*-butyl-*N*-(3,5-di-*tert*-butyl-2-hydroxyphenyl)-*o*-iminobenzoquinone **(IBQ-AP)H**: the methanol solution (30 ml) of 4,6-di-*tert*-butyl-*o*-aminophenol [47] (1 g, 4.5 mmol) was added to a methanol solution (30 ml) of 3,5-di-*tert*-butyl-*o*-benzoquinone (1 g, 4.5 mmol) at ambient temperature. The mixture color turned deep violet. The reaction solution was kept for 0.5 h at RT and then it was stored at −18 °C for a night. The dark violet precipitate was filtered and dried on air. Yield is 1.6 g (83.9%). ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C, TMS, δ, ppm): 1.25 (s, 18H, 2 *t*-Bu); 1.37 (s, 18H, *t*-Bu); 4.88 (v.br.s, 1H, OH); 6.88 (br.s, 2H, C_6H_2); 7.16 (br.s, 2H, C_6H_2). The synthesis of amino-bis-(3,5-di-*tert*-butyl-2-hydroxyphenyl) ligand **(AP-AP)H_3**: the mixture of 4,6-di-*tert*-butyl-*o*-aminophenol [47] (1 g, 4.5 mmol) and 3,5-di-*tert*-butyl-*o*-benzoquinone (1 g, 4.5 mmol) in 50 ml of methanol was stirred at RT for 15 min and then 0.5 ml of hydrazine hydrate was added to this solution. After vigorous boiling was complete, bright-yellow solution was diluted with 5 ml of water and allowed to stay at −18 °C for a night. Yield is 1.55 g (80.4%). ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C, TMS, δ, ppm): 1.22 (s, 18H, 2 *t*-Bu); 1.46 (s, 18H, *t*-Bu); 5.33 (br.s, 1H, NH); 5.46 (br.s, 2H, 2 OH); 6.73 (br.s, 2H, C_6H_2); 7.01 (br.s, 2H, C_6H_2).

Bruker AVANCE DPX-200 spectrometer was used for recording the ^{1}H, ^{13}C, ^{13}C DEPT NMR spectra. Chemical shifts for ^{1}H and ^{13}C spectra were referenced internally according to the residual solvent resonances and reported relative to TMS; $CDCl_3$ was used as solvent. Infrared spectra were recorded on a Perkin–Elmer FT-IR spectrometer in Nujol mulls and reported in cm^{-1}.

3.2. X-ray diffraction studies

X-ray diffraction data for **1** and **5** were collected using Oxford Diffraction (Gemini S) diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) and with CCD detector Sapphire III in the ω-scan mode (hemisphere with max $2\theta = 61°$ resolution, exposure 10 sec on each frame). X-ray data on samples **1** and **5** were collected at temperatures 298 and 100 K, correspondingly. The crystal structure was solved by direct methods (SHELX97) [48]

Table 3
Crystallographic data of **1** and **5**.

	Compound **1**	Compound **5**
Empirical formula	$C_{32}H_{52}NOSb$	$C_{32}H_{50}NO_2Sb$
Formula weight	588.50	602.48
Temperature (K)	298(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	*C2/c*	*P21/c*
Unit cell dimensions	a = 27.7750(9) Å α = 90.00° b = 11.6703(3) Å β = 96.688(3)° c = 19.6418(5) Å γ = 90.00°	a = 11.4101(2) Å α = 90.00° b = 13.7573(2) Å β = 91.7856(13)° c = 19.9503(3) Å γ = 90.00°
Volume (Å^3)	6323.4(3)	3130.12(9)
Z	8	4
D_{calc} (mg/m^3)	1.236	1.278
Absorption coefficient (mm^{-1})	0.895	0.908
F(0 0 0)	2480	1264
Crystal size (mm^3)	0.4 × 0.25 × 0.1	0.3 × 0.25 × 0.1
θ Range for data collection	3.35–30.51°	3.13–30.51°
Completeness to Θ = 30.51	99.8%	99.3%
Reflections collected	9645	9499
Independent reflections	6459 [R_{int} = 0.0547]	8299 [R_{int} = 0.0173]
Absorption correction	SADABS	SADABS
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	9645/0/319	9499/0/526
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0407, wR_2 = 0.0640	R_1 = 0.0257, wR_2 = 0.0565
R indices (all data)	R_1 = 0.0873, wR_2 = 0.0725	R_1 = 0.0336, wR_2 = 0.0583
Goodness-of-fit (GOF) on F^2	0.965	1.090
Largest difference in peak and hole (e Å^{-3})	0.683; −0.683	0.580; −0.475

and refined by full matrix method (WINGX and SHELX97) [49]. The reflection data were processed using the analytical absorption correction algorithm [50]. All non-hydrogen atoms were refined with anisotropic correction. The some part of H atoms were placed in calculated positions and refined in the "riding-model" (U_{iso}(H) = 1.2 U_{eq}(carbon) Å^2 for aromatic hydrogen and 1.5 U_{eq}(carbon) Å^2 for alkyl hydrogen), and the another part was located from Fourier synthesis and refined isotropically [48]. The follow minimal R_1-factors obtained for **1** and **5** correspond to R_1 = 0.0407 and R_1 = 0.0257.

There are no solvent molecules in crystals of **1** and **5** were found. Table 3 summarizes the crystal data and some details of the data collection and refinement for **1** and **5**. Selected bond distances and angles are given in Tables 1 and 2, respectively.

3.3. Preparation of complexes

3.3.1. (4,6-Di-tert-butyl-N-(2,6-di-iso-propylphenyl)-o-amidophenolato)triethylantimony (**1**) and (4,6-di-tert-butyl-N-(2,6-dimethylphenyl)-o-amidophenolato)triethylantimony (**2**)

Method 1: The THF solution of sodium *o*-amidophenolate (prepared from 0.379 g (1 mmol) of IBQ-iPr (for **1**) or 0.323 g (1 mmol) of IBQ-Me (for **2**) and an excessing Na in 20 ml THF) was added slowly with an extensive stirring to a THF solution of Et_3SbBr_2 (0.369 g, 1 mmol). After addition was complete, the reaction mixture was heated at 50–60 °C for 30 min. Then THF was replaced with pentane (~25 ml), filtered to remove NaBr residue and concentrated to half initial volume. The storing of solution at −18 °C for 1–2 day allowed to obtain the yellow microcrystalline products which were recrystallized from pentane to give X-ray suitable yellow crystals of **1** (0.520 g, 88.4%) or **2** (0.490 g, 92.1%).

*(AP-iPr)SbEt$_3$ (**1**)*: IR (Nujol, KBr, ν, cm^{-1}): 1566 m, 1464 m, 1440 s, 1419 s, 1356 w, 1338 m, 1316 m, 1287 s, 1252 vs, 1239 m, 1200 m, 1180 w, 1103 m, 1080 w, 1050 w, 1040 w, 1027 m, 992 s, 935 w, 920 w, 901 m, 850 m, 826 w, 803 s, 772 m, 760 w, 712 w, 688 w, 670 w, 666 w, 654 w, 606 w, 585 w, 543 w, 531 w, 518 w, 506 m, 478 m, 452 w, 425w. ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C, TMS, δ, ppm): 1.03 (d, $^3J_{HH}$ = 6.9 Hz, 6H, 2 CH(CH_3)$_2$); 1.09 (s, 9H, *t*-Bu); 1.18 (d, $^3J_{HH}$ = 6.9 Hz, 6H, 2 CH(CH_3)$_2$); 1.29 (t, $^3J_{HH}$ = 7.6 Hz, 9H, 3 CH_2CH_3); 1.45 (s, 9H, *t*-Bu); 1.61 (q, $^3J_{HH}$ = 7.6 Hz, 6H, 3 CH_2CH_3); 3.16 (sept., $^3J_{HH}$ = 6.9 Hz, 2H, 2 $CH(CH_3)_2$); 5.72 (d, $^4J_{HH}$ = 2.3 Hz, 1H, C_6H_2); 6.55 (d, $^4J_{HH}$ = 2.3 Hz, 1H, C_6H_2); 7.16–7.33 (m, 3H, C_6H_3). ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C, δ, ppm): 9.28, 18.88, 23.90, 25.69, 27.61, 29.66, 31.77, 34.18, 34.64, 107.18, 111.06, 123.92, 127.06, 130.27, 135.80, 136.69, 139.05, 146.40, 149.09. ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, 20 °C, δ, ppm): 9.28 (s, 3 CH_2CH_3), 18.88 (s, 3 CH_2CH_3), 23.90 and 25.69 (both s, both 2 CH(CH_3)$_2$), 27.61 (s, 2 $CH(CH_3)_2$), 29.67 and 31.77 (both s, both 3 C(CH_3)$_3$), 107.18 (s, Ar), 111.06 (s, Ar), 123.92 (s, Ar), 127.06 (s, Ar). Anal. Calc. (%) for $C_{32}H_{52}NOSb$ (588.52): C, 65.31; H, 8.91; N, 2.38; Sb, 20.69. Found: C, 65.47; H, 8.99; N, 2.04; Sb, 20.97%.

*(AP-Me)SbEt$_3$ (**2**)*: IR (Nujol, KBr, ν, cm^{-1}): 1563 m, 1443 s, 1416 s, 1356 w, 1331 m, 1288 s, 1246 vs, 1202 m, 1163 w, 1119 w, 1096 w, 1026 w, 991 s, 975 w, 920 w, 897 m, 849 m, 827 w, 770 m, 760 w, 742 w, 708w, 695 w, 667 w, 651 w, 605 w, 540 w, 532 w, 514 w, 505 m, 475 m, 448 w. ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C, TMS, δ, ppm): 1.11 (s, 9H, *t*-Bu); 1.27 (t, $^3J_{HH}$ = 7.8 Hz, 9H, 3 CH_2CH_3); 1.45 (s, 9H, *t*-Bu); 1.64 (q, $^3J_{HH}$ = 7.8 Hz, 6H, 3 CH_2CH_3); 2.18 (s, 6H, 2 CH_3); 5.74 (d, $^4J_{HH}$ = 2.3 Hz, 1H, C_6H_2); 6.62 (d, $^4J_{HH}$ = 2.3 Hz, 1H, C_6H_2); 7.10–7.14 (m, 3H, C_6H_3). ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C, δ, ppm): 9.35, 18.54, 19.09, 29.62, 31.79, 34.12, 34.65, 105.09, 111.46, 126.20, 128.53, 130.48, 134.66, 136.29, 138.81, 141.94, 146.83. ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, 20 °C, δ, ppm): 9.35 (s, 3 CH_2CH_3), 18.54 (s, 2 CH_3), 19.09 (s, 3 CH_2CH_3), 29.62 and 31.79 (both s, both 3 C(CH_3)$_3$), 105.09 (s, Ar), 111.46 (s, Ar), 126.20 (s, Ar), 128.53 (s, Ar). Anal. Calc. (%) for $C_{28}H_{44}NOSb$ (532.41): C, 63.16; H, 8.33; N, 2.63; Sb, 22.87. Found: C, 63.01; H, 8.09; N, 2.77; Sb, 22.28%.

Method 2: The sample of Et_3Sb (0.1 M toluene solution) was added with stirring to a solution of IBQ-iPr (0.250 g, 0.66 mmol) or IBQ-Me (0.220 g, 0.68 mmol) in toluene (15–20 ml) till color change from cherry-red to yellow was complete. Toluene was evaporated under vacuum, and the solid residue was dissolved in pentane (15 ml). After the slow evaporation of pentane followed by cooling of solution to −12 °C and storing at this temperature for 1 day allowed to isolate complex **1** or **2**, correspondingly, as an yellow crystalline solids (0.372 g, 95.8% for **1** and 0.341 g, 94.2% for **2**). The spectroscopic characteristics of the products prepared by methods 1 and 2 are identical.

3.3.2. (3,6-Di-tert-butyl-catecholato)triethylantimony(V) (**3**)

The sample of complex **3** was synthesized by procedure similar to method 2 for **1** and **2**; complex was isolated as the viscous pale yellow oil which crystallizes with time. It can be easily stored at room temperature under inert atmosphere. Yield was 93%. IR (Nujol, KBr, ν, cm^{-1}): 1586 w, 1572 w, 1534 w, 1484 m, 1451 m, 1403 s, 1352 m, 1282 s, 1258 s, 1241 s, 1203 s, 1145 m, 1026 m, 976 s, 941 s, 925 m, 810 m, 787 s, 710 m, 689 s, 651 s, 589 m, 541 w, 515 m, 496 w, 465 m, 444 m. ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C, TMS, δ, ppm): 1.39 (s, 18H, 2 t-Bu), 1.41 (t, $^3J_{HH}$ = 7.9 Hz, 9H, 3 CH_2CH_3), 1.90 (q, $^3J_{HH}$ = 7.9 Hz, 6H, 3 CH_2CH_3), 6.54 (s, 2H, C_6H_2). ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C, δ, ppm): 9.10, 20.06, 29.34, 34.08, 113.38, 131.35, 140.06. ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, 20 °C, δ, ppm): 9.10 (s, 3 CH_2CH_3), 20.06 (s, 3 CH_2CH_3), 29.34 (s, 2 C(CH_3)$_3$), 113.38 (s, Ar). Anal. Calc. (%) for $C_{20}H_{35}O_2Sb$ (429.25): C, 55.96; H, 8.22; Sb, 28.37. Found: C, 56.07; H, 8.39; Sb, 28.65%.

*3.3.3. Amino-bis-(3,5-di-tert-butyl-phenolate-2-yl)triethylantimony(V) (**4**)*

Method 1: The solution of amino-bis-phenol (AP-AP)H_3 (0.212 g, 0.5 mmol, toluene 30 ml) was added dropwise to a solution of Et_3SbBr_2 (0.185 g, 0.5 mmol) and Et_3N (0.14 ml, 1 mmol) in toluene (20 ml) at ~0 °C. After the addition was complete, reaction mixture was filtered to remove colorless precipitate of $[Et_3NH]Br$. The change of the solvent with hexane and storing this solution at −18 °C for 1 day allowed colorless microcrystalline solid product. Yield is 0.197 g (62.4%). This complex should be stored in vacuo under low temperature. IR (Nujol, KBr, ν, cm^{-1}): 3158 s, 1603 w, 1563 w, 1482 s, 1454 s, 1445 s, 1415 m, 1377 m, 1360 m, 1302 s, 1284 s, 1269 w, 1240 m, 1202 s, 1164 w, 1129 m, 1034 w, 1020 m, 980 m, 936 w, 914 m, 878 m, 857 w, 834 s, 810 w, 785 m, 751 s, 707 s, 667 w, 645 w, 584 w, 541 w, 519 s, 510 w, 487 m, 475 m, 439 w, 405 w. ^1H NMR (200 MHz, $CDCl_3$, 20 °C, TMS, δ, ppm): 1.16 (t, $^3J_{HH}$ = 7.9 Hz, 6H, 2 CH_2CH_3), 1.26 and 1.35 (s, both 18 H, t-Bu), 1.42 (q, $^3J_{HH}$ = 7.9 Hz, 4H, 2 CH_2CH_3), 1.61 (t, $^3J_{HH}$ = 7.8 Hz, 3H, CH_2CH_3), 1.90 (q, $^3J_{HH}$ = 7.8 Hz, 2H, CH_2CH_3), 4.96 (br.s, 1H, NH), 7.08 and 7.21 (both d, $^4J_{HH}$ = 2.4 Hz, both 2H, 2 C_6H_2). ^1H NMR (400 MHz, benzene-d, 20 °C, TMS, δ, ppm): 1.06 (t, $^3J_{HH}$ = 7.9 Hz, 6H, 2 CH_2CH_3); 1.21 (q, 4H, $^3J_{HH}$ = 7.9 Hz, 2 CH_2CH_3); 1.32 (s, 18H, 2 t-Bu); 1.56 (s, 18H, 2 t-Bu); 1.69 (t, J = 7.9 Hz, 3H, CH_2CH_3); 1.89 (q, 2H, $^3J_{HH}$ = 7.9 Hz, CH_2CH_3), 4.38 (s, 1H, NH); 7.09 (d, $^4J_{HH}$ = 2.0 Hz, 2H, C_6H_2); 7.32 (d, $^4J_{HH}$ = 2.0 Hz, 2H, C_6H_2). ^{13}C NMR (101 MHz, benzene-d, 20 °C, δ, ppm): 9.03, 9.18, 9.72, 10.18, 16.69, 22.86, 29.41, 29.94, 31.69, 34.11, 35.33, 118.60, 122.87, 129.78, 137.53, 137.64, 151.86. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, 20 °C, δ, ppm): 8.16 (3 CH_2CH_3), 23.41 (3 CH_2CH_3), 29.56 and 31.87 (both 2C$(CH_3)_3$), 107.99 (Ar), 13.70 (Ar). Anal. Calc. (%) for $C_{34}H_{56}NO_2Sb$ (632.57): C, 64.56; H, 8.92; N, 2.21; Sb, 19.25. Found: C, 63.91; H, 8.79; N, 2.07; Sb, 18.98%.

Method 2: The solution of 4,6-di-*tert*-butyl-*N*-(3,5-di-*tert*-butyl-2-hydroxyphenyl)-*o*-iminobenzoquinone **(IBQ-AP)H** (254 mg, 0.6 mmol, toluene 30 ml) was slowly added to a toluene solution of $SbEt_3$ (125 g, 0.6 mmol, toluene 20 ml) at low temperature (~0 °C) with the extensive stirring. After the complete disappearance of violet color of the solution, the solvent was removed off by evaporation, and the pale yellow residue was dissolved in hexane. This solution was allowed to stay at −18 °C for a night after that the pale yellow crystalline powder was collected by filtration. Yield is 0.25 g (65.9%).

*3.3.4. Amido-bis-(3,5-di-tert-butyl-phenolate-2-yl)diethylantimony(V) (**5**)*

Method 1: The exposure of the solution of **4** to air for a 1 h leads to yellow complex **5** with a nearly quantitative yield (~98%).

Method 2: The solution of $SbEt_3$ (105 g, 0.5 mmol, toluene 20 ml) was added dropwise to a solution of 4,6-di-*tert*-butyl-*N*-(3,5-di-*tert*-butyl-2-hydroxyphenyl)-*o*-iminobenzoquinone **(IBQ-AP)H** (212 mg, 0.5 mmol, toluene 25 ml). The violet color was disappeared and toluene was changed with hexane. The yellow residue precipitated after solution cooling was recrystallized from another hexane portion. The storage of this solution at −18 °C for 3 days gave white X-ray quality crystals which were collected by filtration and dried in vacuo. Yield is 0.265 g (88.0%). IR (Nujol, KBr, ν, cm^{-1}): 1726 w, 1713 w, 1587 m, 1568 s, 1480 s, 1445 s, 1416 m, 1391 m, 1377 m, 1346 s, 1313 m, 1282 s, 1260 w, 1243 s, 1218 m, 1204 s, 1162 w, 1130 m, 1052 s, 1022 m, 1012 s, 959 s, 931 w, 913 w, 861 s, 841 s, 822 w, 754 m, 739 w, 703 w, 688 w, 679 w, 642 s, 601 w, 548 s, 529 m, 504 w, 451 w, 423 w, 414 w, 403 w. ^1H NMR (200 MHz, $CDCl_3$, 20 °C, TMS, δ, ppm): 1.38 (s, 18 H, 2 t-Bu); 1.43 (s, 18 H, 2 t-Bu); 1.46 (t, $^3J_{HH}$ = 7.90 Hz, 6H, 2 CH_2CH_3); 2.30 (q, $^3J_{HH}$ = 7.9 Hz, 4H, 2 CH_2CH_3); 6.84 (d, $^4J_{HH}$ = 2.2 Hz, 2H, 2 C_6H_2); 7.78 (d, $^4J_{HH}$ = 2.2 Hz, 2H, 2 C_6H_2). ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C, δ, ppm): 8.13, 23.38, 29.56, 31.86, 34.63, 34.93, 107.98, 113.68, 132.03, 133.66, 139.30, 145.71. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, 20 °C, δ, ppm): 8.13 (2 CH_2CH_3), 23.38 (2 CH_2CH_3), 29.56 (2 C$(CH_3)_3$), 31.86 (2 C$(CH_3)_3$), 107.98 (s, Ar), 113.68 (s, Ar). Anal. Calc. (%) for $C_{32}H_{50}NO_2Sb$ (602.463): C, 63.79; H, 8.36; N, 2.32; Sb, 20.21. Found: C, 64.06; H, 8.12; N, 2.23; Sb, 20.51%.

*3.3.5. Reaction of **1** and **2** with molecular oxygen*

The solution of **1** or **2** in $CDCl_3$ (0.015 M) was exposed to air in NMR tube and a steam of fresh air was passed through solution. ^1H NMR spectra were recorded each hour during 8 h. Then tube was degassed by the five time repeating cycle "freeze-pump-warm" to remove air and then ^1H NMR spectra were recorded again to show the formation of initial complexes **1** or **2**, correspondingly.

*[(L-iPr)O_2]$SbEt_3$ (**6**)*: ^1H NMR (200 MHz, $CDCl_3$, 20 °C, TMS, δ, ppm): 0.99 (s, 9H, *t*-Bu); 1.36 (s, 9H, *t*-Bu); 1.28 (t, $^3J_{HH}$ = 7.9 Hz, 9H, 3 CH_2CH_3); 2.47 (q, $^3J_{HH}$ = 7.9 Hz, 6H, 3 CH_2CH_3); 2.83 (sept., $^3J_{HH}$ = 6.8 Hz, 1H, $CH(CH_3)_2$); 3.45 (sept., $^3J_{HH}$ = 6.8 Hz, 1H, $CH(CH_3)_2$); 6.36 (d, $^4J_{HH}$ = 1.7 Hz, 1H, C_6H_2); 6.42 (d, $^4J_{HH}$ = 1.7 Hz, 1H, C_6H_2); 6.97–7.30 (m, 3H, C_6H_3). Methyl groups of *i*Pr were difficult to determine.

*[(L-Me)O_2]$SbEt_3$ (**7**)*: ^1H NMR (200 MHz, $CDCl_3$, 20 °C, TMS, δ, ppm): 1.01 (s, 9H, *t*-Bu); 1.29 (t, $^3J_{HH}$ = 7.9 Hz, 9H, 3 CH_2CH_3); 1.35 (s, 9H, *t*-Bu); 2.46 (q, $^3J_{HH}$ = 7.9 Hz, 6H, 3 CH_2CH_3); 2.08 and 2.21 (both s, both 3H, 2 CH_3); 5.37 (d, $^4J_{HH}$ = 1.6 Hz, 1H, C_6H_2); 6.35 (d, $^4J_{HH}$ = 1.6 Hz, 1H, C_6H_2); 6.9–7.1 (m, 3H, C_6H_3).

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Appendix A. Supplementary data

CCDC 716050 and 716049 contains the supplementary crystallographic data for complexes **1** and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.06.027.

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