Journal of Organometallic Chemistry 695 (2010) 530–536

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Antimony(V) catecholato complexes based on 4,5-dialkylsubstituted *o*-benzoquinone. The spectroscopic and electrochemical studies. Crystal structure of $[Ph_4Sb]^+[Ph_2Sb(4,5\text{-}Cat)_2]^-$

Andrey I. Poddel'sky [a,*], Ivan V. Smolyaninov [b], Nikolay V. Somov [c], Nadezhda T. Berberova [b], Vladimir K. Cherkasov [a], Gleb A. Abakumov [a]

[a] G.A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Tropinina 49, 603950 Nizhniy Novgorod, GSP-445, Russia
[b] Southern Scientific Center, Russian Academy of Sciences, 41 Chekhova Street, 344006 Rostov-on-Don, Russia
[c] Nizhniy Novgorod State University, Physical Faculty, Building 3, Gagarina Avenue 23, 603950 Nizhniy Novgorod, Russia

ARTICLE INFO

Article history:
Received 29 May 2009
Received in revised form 3 November 2009
Accepted 16 November 2009
Available online 23 November 2009

Keywords:
Antimony
o-Quinone
Catecholate
NMR spectroscopy
X-ray structure
Electrochemistry

ABSTRACT

Triphenylantimony(III) and triethylantimony(III) readily react with 4,5-(1,1,4,4-tetramethyl-butane-1,4-diyl)-*o*-benzoquinone to form catecholato complexes $R_3Sb(4,5\text{-}Cat)$ (R = Ph (**1**), Et (**2**); 4,5-Cat is dianionic 4,5-(1,1,4,4-tetramethyl-butane-1,4-diyl)-catecholate). In polar solvents ($CHCl_3$, acetone) complex **1** transforms easily to ionic complex compound $[Ph_4Sb]^+[Ph_2Sb(4,5\text{-}Cat)_2]^-$ (**3**) with diphenyl-bis-[4,5-(1,1,4,4-tetramethyl-butane-1,4-diyl)-catecholato]antimony(V) complex anion. Complexes were characterized by IR, ^1H, ^{13}C NMR spectroscopy, cyclic voltammometry. Molecular structure of **3**·$CHCl_3$ was confirmed by X-ray analysis. Cyclic voltammometry of **1** and **3** shows that both complexes undergo reversible one-electron oxidation to quite stable paramagnetic *o*-semiquinonato species $[Ph_3Sb(4,5\text{-}SQ)]^+$ and $[Ph_2Sb(4,5\text{-}SQ)(4,5\text{-}Cat)]$ (0.75 and 0.49 V in CH_2Cl_2 vs. Ag/AgCl/KCl, respectively).

1. Introduction

At the present time the coordination and organometallic chemistry of antimony(III, V) becomes a dynamic developed area of chemistry. Organoantimony compounds attract the scientists' interest owing to their activity in quite a number of reactions [1–6], fine organic synthesis [7–13]. Antimony organics have found their application in pharmacy and medicine (as the medicaments, antioxidants), agriculture (fungicides), etc. [14–16]. The combination of antimony and redox-active *o*-quinone type ligands have revealed next one unusual property of non-transition metal complexes – the reversible binding of molecular oxygen [17–19]. These circumstances cause our interest to new antimony complexes with *o*-quinonato type ligands which can serve as oxidizing agents, dioxygen carriers etc.

In our previous investigations we have synthesized a number of triphenylantimony(V) catecholates of different sterically hindered di-tert-butyl-*o*-quinones [18,20,21]. It was shown that the structure and stability of complexes formed depends on sterical shielding of Cat ligand as well as redox-potentials of Cat ligand [21]. For example, the application of catecholates with electron-donor groups 4-methoxy- or 4,5-dimethoxy-3,6-di-tert-butyl-catecholate (4-MeO- and 4,5-$(MeO)_2$-3,6-DBCat) allows these complexes to reversibly trap molecular oxygen [18], while the insertion of different acceptors to Cat ligand results in air-stable catecholates [20,21]. What about sterical factors, in most cases catecholates used are derivatives of sterically hindered 3,6-di-tert-butyl-*o*-benzoquinone or 3,5-di-tert-butyl-*o*-benzoquinone. Here we report synthesis and structure of new antimony(V) catecholates based on 4,5-dialkylsubstituted *o*-benzoquinone 4,5-(1,1,4,4-tetramethyl-butane-1,4-diyl)-*o*-benzoquinone which has not hindrances at 3 and 6 positions of Cat ligand and it leads to some chemical features of complexes formed. We can expect some reactivity of complexes in dioxygen binding reaction and their ability to undergo the rearrangement to form bis-catecholato-diphenylantimonato(V) anionic salts.

2. Experimental

All manipulations were carried out under an air-free atmosphere. All solvents were purified using standard technique [22]. Anhydrous $SbCl_3$, $SbPh_3$ and EtBr were purchased. $SbEt_3$ [23], 4,5-(1,1,4,4-tetramethyl-butane-1,4-diyl)-*o*-benzoquinone [24] were prepared according to reported procedures.

* Corresponding author. Fax: +7 831 462 74 97.
E-mail address: aip@iomc.ras.ru (A.I. Poddel'sky).

0022-328X/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2009.11.022

2.1. Synthesis

2.1.1. (4,5-(1,1,4,4-tetramethyl-butane-1,4-diyl)-catecholato)triphenylantimony(V) (**1**)

A toluene solution of 4,5-(1,1,4,4-tetramethyl-butane-1,4-diyl)-*o*-benzoquinone (0.219 g, 1 mmol, 20 ml) was added with a continuous stirring to a toluene solution of $SbPh_3$ (0.354 g, 1 mmol, 15 ml). After the solution color changed to bright yellow, toluene was replaced with hexane. Storing of the solution at −18 °C allowed to form precipitate bright yellow powder which was filtered off and dried in vacuo. Yield is 0.45 g (78.7%), m.p. 129–133 °C. *Anal.* Calc. for $C_{32}H_{33}O_2Sb$: C, 67.27; H, 5.82; Sb, 21.31. Found: C, 66.98; H, 5.90; Sb, 21.48%. IR (nujol, *ν*, cm^{-1}): 1604 w, 1570 w, 1492 s, 1458 m, 1435 s, 1402 w, 1377 m, 1360 m, 1340 m, 1307 w, 1254 s, 1207 m, 1181 m, 1158 m, 1099 w, 1084 w, 1067 m, 1022 m, 997 m, 889 m, 870 s, 814 s, 782 w, 741 s, 693 s, 663 w, 654 w, 616 w, 588 m, 567 m, 543 w, 527 m, 453 s. ^{1}H NMR ($CDCl_3$, *δ*, ppm): 1.24 (s, 12H, $4CH_3$), 1.64 (s, 4H, $–CH_2–CH_2–$), 6.89 (s, 2H, C_6H_2), 7.38–7.52 (m, 9H, $SbPh_3$), 7.70–7.77 (m, 6H, $SbPh_3$). ^{1}H NMR (d^8-acetone, *δ*, ppm): 1.20 (s, 12H, $4CH_3$), 1.62 (s, 4H, $–CH_2–CH_2–$), 6.69 (s, 2H, C_6H_2), 7.42–7.58 (m, 9H, $SbPh_3$), 7.70–7.86 (m, 6H, $SbPh_3$). ^{13}C NMR ($CDCl_3$, *δ*, ppm): 32.11 (CH_3), 33.90 ($C(CH_3)_2$), 35.52 ($–CH_2–CH_2–$), 109.46 (*C*H of Ar), 129.22 ($SbPh_3$), 131.15 ($SbPh_3$), 134.71 (Ar), 135.03 ($SbPh_3$), 137.71 ($SbPh_3$), 145.39 (Ar). ^{13}C{^{1}H} NMR ($CDCl_3$, *δ*, ppm): 32.11, 35.52, 109.46, 129.22, 131.15, 135.03. ^{13}C NMR (d^8-acetone, *δ*, ppm): 32.55 (CH_3), 34.40 ($C(CH_3)_2$), 36.40 ($–CH_2–CH_2–$), 109.99 (*C*H of Ar), 129.80 ($SbPh_3$), 131.56 ($SbPh_3$), 134.74 (Ar), 135.75 ($SbPh_3$), 140.99 ($SbPh_3$), 146.68 (Ar). ^{13}C{^{1}H} NMR ($CDCl_3$, *δ*, ppm): 32.55, 36.40, 109.99, 129.80, 131.56, 135.75.

2.1.2. (4,5-(1,1,4,4-tetramethyl-butane-1,4-diyl)-catecholato)triethylantimony(V) (**2**)

Complex **2** was prepared by the same method as reported for **1** from 0.21 g (1 mmol) of $SbEt_3$ and 0.22 g (1 mmol) of 4,5-(1,1,4,4-tetramethyl-butane-1,4-diyl)-*o*-benzoquinone. Complex was isolated from pentane. Yield is 0.28 g (65.6%), decomp. >100 °C. *Anal.* Calc. for $C_{20}H_{33}O_2Sb$: C, 56.23; H, 7.79; Sb, 28.50. Found: C, 56.71; H, 7.90; Sb, 27.88%. IR (nujol, *ν*, cm^{-1}): 1608 w, 1589 w, 1513 w, 1493 s, 1463 m, 1404 w, 1364 w, 1341 w, 1318 w, 1273 s, 1252 s, 1206 m, 1160 m, 1150 m, 1084 w, 1020 m, 989 w, 890 w, 876 w, 860 m, 812 m, 805 m, 722 m, 690 w, 557 w, 407 m. ^{1}H NMR ($CDCl_3$, *δ*, ppm): 1.22 (s, 12H, $4CH_3$), 1.39 (t, $^4J_{HH}$ = 7.9 Hz, 9H, 3 CH_3CH_2), 1.63 (s, 4H, $–CH_2–CH_2–$), 1.96 (q, $^4J_{HH}$ = 7.9 Hz, 6H, 3 CH_3CH_2), 6.71 (s, 2H, C_6H_2). ^{13}C NMR ($CDCl_3$, *δ*, ppm): 9.13 (CH_3CH_2), 19.99 (CH_3CH_2), 32.09 (CH_3), 33.85 ($C(CH_3)_2$), 35.57 ($–CH_2–CH_2–$), 108.91 (*C*H of Ar), 134.09 (Ar), 145.89 (Ar). ^{13}C{^{1}H} NMR ($CDCl_3$, *δ*, ppm): 9.13, 19.99, 32.09, 35.57, 108.91.

2.1.3. Tetraphenylstibonium(V) diphenyl-bis-[4,5-(1,1,4,4-tetramethyl-butane-1,4-diyl)-catecholato]antimony(V) (**3**)

A sample of complex **1** (0.05 g, 0.087 mmol) was dissolved in $CHCl_3$ (10 ml) and left untouched for a week. The yellow color of solution disappeared slowly with concomitant formation of nearly colorless crystals suitable for X-ray analysis. Yield of **3**·$CHCl_3$ is 0.053 g (96%). *Anal.* Calc. for $C_{65}H_{67}Cl_3O_4Sb_2$: C, 61.86; H, 5.35; Cl, 8.43; Sb, 19.29. Found: C, 61.53; H, 5.27; Cl, 8.01; Sb, 19.43%.

IR (nujol, *ν*, cm^{-1}): 1604 w, 1490 m, 1462 m, 1437 m, 1377 m, 1356 w, 1340 w, 1306 w, 1246 s, 1203 w, 1183 w, 1156 w, 1102 w, 1077 w, 1066 m, 1019 w, 995 m, 929 w, 891 w, 871 s, 861 s, 810 s, 781 w, 731 s, 700 s, 689 s, 661 w, 657 w, 639 w, 583 m, 567 w, 543 w, 518 w, 456 s, 444 s, 409 w.

^{1}H NMR (d^8-acetone, *δ*, ppm): 1.07 (s, 6H, 2 CH_3), 1.10 (s, 6H, 2 CH_3), 1.16 (s, 6H, 2 CH_3), 1.20 (s, 6H, 2 CH_3), 1.56 (s, 8H, $–CH_2–CH_2–$), 6.29 (s, 2H, C_6H_2), 6.63 (s, 2H, C_6H_2), 7.14–7.22 (m, 6H, 2 *p*-H, 4 *o*-H of $SbPh_2$), 7.68-7.85 (m, 16H, 4 *m*-H of $SbPh_2$ and 4 *p*-H, 8 *o*-H of $SbPh_4$), 7.89–7.96 (m, 8H, *m*-H of $SbPh_4$).

^{13}C NMR (d^8-acetone, *δ*, ppm): 32.51, 32.58, 32.61, 32.78 (all CH_3), 34.19 and 34.21 (both $C(CH_3)_2$), 36.72 and 36.74 ($–CH_2–CH_2–$), 110.25 and 110.34 (both *C*H of Ar), 128.17 (*o*-*C* of $SbPh_2$), 128.81 (*p*-*C* of $SbPh_2$), 131.51 (Ar), 131.86 (*m*-*C* of $SbPh_4^+$), 133.12 (Ar), 134.49 (*p*-*C* of $SbPh_4^+$), 134.73 (*m*-*C* of $SbPh_2$), 135.73 (*i*-*C* of $SbPh_2$), 136.62 (*o*-*C* of $SbPh_4^+$), 149.09 (Ar), 150.36 (Ar), 151.92 (*i*-*C* of $SbPh_4^+$). ^{13}C{^{1}H} NMR ($CDCl_3$, *δ*, ppm): 32.51, 32.58, 32.61, 32.78, 36.72, 36.74, 110.25, 110.34, 128.17, 128.81, 131.86, 134.49, 134.73, 136.62.

2.2. Physical measurements

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; $CDCl_3$ and d^8-acetone were used as solvents. Infrared spectra were recorded on a Perkin–Elmer FT-IR spectrometer as Nujol mulls and are reported in cm^{-1}.

Electrochemical studies were carried out using an IPC-pro potentiostate in threeelectrode mode. The glassy carbon (*d* = 2 mm) disk was used as working electrode; the auxiliary electrode was a platinum-flag electrode. The reference electrode was an Ag/AgCl/KCl (sat.) with watertight diaphragm. All measurements were carried out under argon. The samples were dissolved in the pre-deaerated solvent. The rate scan was 200 mV s^{-1}.The supporting electrolyte 0.1 M $[(n\text{-}Bu)_4N]ClO_4$ (99%, "Acros") was doubly recrystallized from aqueous ethanol and then it was dried in vacuum at 50 °C for 48 h.

2.3. Crystal structure determination

X-ray diffraction data for **3**·$CHCl_3$ were collected by 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 s on each frame). The crystal structure was solved by direct methods (SHELX97) [25] and refined by full matrix method (WINGX and SHELX97) [26]. The reflection data were processed by using the analytical absorption correction algorithm [27]. All non-hydrogen atoms were refined with anisotropic correction. All 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). The follow minimal R_1-factor was obtained for **3**·$CHCl_3$ is $R_1 = 0.0295$. The selected bond lengths and angles are listed in Table 1. Crystallographic data on **3**·$CHCl_3$ are given in Table 2.

3. Results and discussion

3.1. Synthesis and characterization

The oxidative addition of 4,5-(1,1,4,4-tetramethyl-butane-1,4-diyl)-*o*-benzoquinone to triphenylstibine or triethylstibine (Scheme 1) proceeds easy with the color change from orange-red (the color of initial quinone) to bright yellow. The reaction product, (4,5-(1,1,4,4-tetramethyl-butane-1,4-diyl)-catecholato)triphenylantimony(V) (**1**), is slightly soluble in a wide number of polar and non-polar solvents.

Complexes were characterized by ^{1}H and ^{13}C NMR-, IR-spectroscopy and an elemental analysis.

Compound **1** was found to be air-stable like the related complex (3,6-di-tert-butyl-catecholato)triphenylantimony [20]. The trie-