Main-Group Chemistry

Reversible Binding of Dioxygen by a Non-Transition-Metal Complex**

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For decades, reversible binding of molecular oxygen to various organic and coordination compounds has remained one of the fundamental problems in chemistry because it concerns a number of biochemical and catalytic processes that occur with the participation of molecular oxygen.[1] Numerous examples of reversible binding of molecular oxygen to transition-metal complexes, thus modeling the active centers in biological oxygen carriers, are known.[2] In these complexes, the binding of oxygen is accompanied, in many cases, by the transfer of electrons from the metal center to the oxygen molecule, and thus the oxidation state of the metal atom changes.

A number of studies concern the problem of reversible binding of oxygen to condensed aromatic compounds to form endoperoxides.[3] Usually in these cases, dioxygen is bound and liberated in a singlet state from the adduct that is formed. Therefore, its activation requires a significant amount of excitation energy.

The reversible addition of molecular oxygen to non-transition-metal and nonmetal organoelemental compounds has not been reported to date. Herein, we describe the first example of reversible binding of dioxygen by a non-transition-metal complex: *o*-amidophenolatotriphenylantimony(v).

The starting complex [4,6-di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)-*o*-amidophenolato]triphenylantimony(v) (**1**) was synthesized by the oxidative addition of 4,6-di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)-*o*-iminobenzoquinone to triphenyl antimony(iii) (Scheme 1). Compound **1** was characterized by NMR, IR, and UV/Vis spectroscopies.

The molecular structure of **1** was determined by X-ray analysis (Figure 1). Single crystals of **1** suitable for X-ray analysis were obtained by slow recrystallization from toluene as a toluene solvate **1**·0.5 $C_6H_5CH_3$. The structure of **1** shows that atom Sb(1) has a distorted tetragonal-pyramidal coordination. The basal plane is formed by oxygen, nitrogen, and two carbon atoms, C(33) and C(39), of phenyl groups that are

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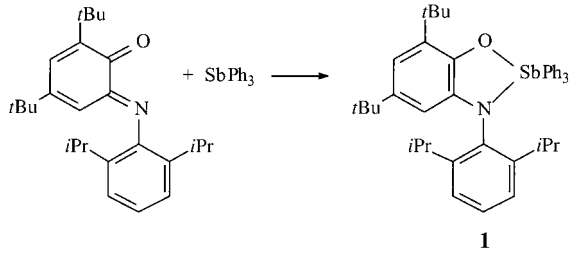
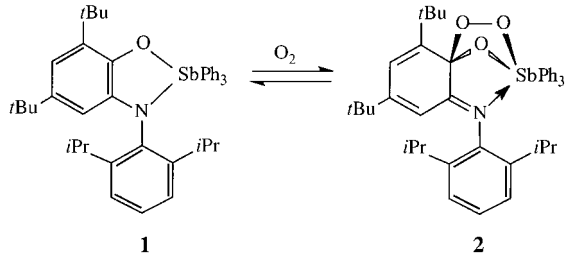


Scheme 1. The synthesis of **1**.



Scheme 2. The interconversion of **1** and **2**.

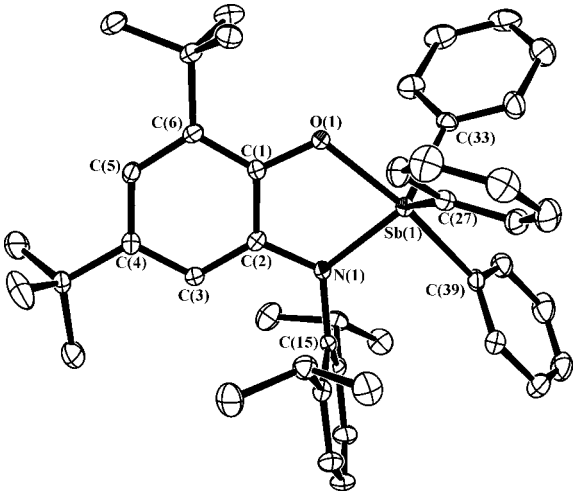


Figure 1. An ORTEP view of **1**, with 30% probability ellipsoids (H atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Sb(1)-O(1) 2.074(2), Sb(1)-N(1) 2.041(3), Sb(1)-C(27) 2.128(4), Sb(1)-C(33) 2.138(4), Sb(1)-C(39) 2.137(4), O(1)-C(1) 1.351(4), N(1)-C(2) 1.408(4), N(1)-C(15) 1.441(4), C(1)-C(2) 1.406(5), C(2)-C(3) 1.382(5), C(3)-C(4) 1.385(5), C(4)-C(5) 1.388(5), C(5)-C(6) 1.396(5), C(1)-C(6) 1.395(5); N(1)-Sb(1)-O(1) 77.83(10), N(1)-Sb(1)-C(27) 116.19(14), O(1)-Sb(1)-C(27) 94.13(13), N(1)-Sb(1)-C(33) 134.40(14), O(1)-Sb(1)-C(33) 84.18(13), C(27)-Sb(1)-C(33) 106.52(16), N(1)-Sb(1)-C(39) 92.60(13), O(1)-Sb(1)-C(39) 164.81(13), C(27)-Sb(1)-C(39) 100.72(15), C(33)-Sb(1)-C(39) 94.56(15).

coordinated to the Sb center. The apical position is occupied by a carbon atom, C(27), of a third phenyl group. The dihedral angle between the C(33)-Sb(1)-C(39) and O(1)-Sb(1)-N(1) planes is 134.2°. The C–C bond lengths in the C(1)–C(6) carbon ring lie in the range 1.385(5)–1.406(5) Å, which indicates that the ring is aromatic. The C–N (1.408(4) Å) and C–O (1.351(4) Å) bond lengths are very close to those found in *N*-phenyl-*o*-amidophenolate ligands in other metal complexes (C–N, 1.38–1.39 Å; C–O, 1.35–1.36 Å)[4] and to that expected for C–O bonds in catecholates (1.35 Å).[5] The Sb–O (2.074(2) Å) and Sb–N (2.041(2) Å) interatomic distances are close to the covalent radii of the corresponding elements.[6] Thus, the structure determination unambiguously shows that the antimony(v) center in **1** is bound to an *o*-amidophenolate dianion and three phenyl groups; this structure is also supported by IR spectroscopic data.

Complex **1** is thermally stable (m.p. 170–171 °C) and air-stable in the solid state. However, in solution, **1** binds molecular oxygen to yield compound **2**, which contains a five-atom trioxastibolane ring (Scheme 2). After prolonged exposure of a solution of complex **1** to air, changes in the corresponding NMR and electronic absorption spectra are observed. In the ^{1}H NMR spectrum (Figure 2), the intensity

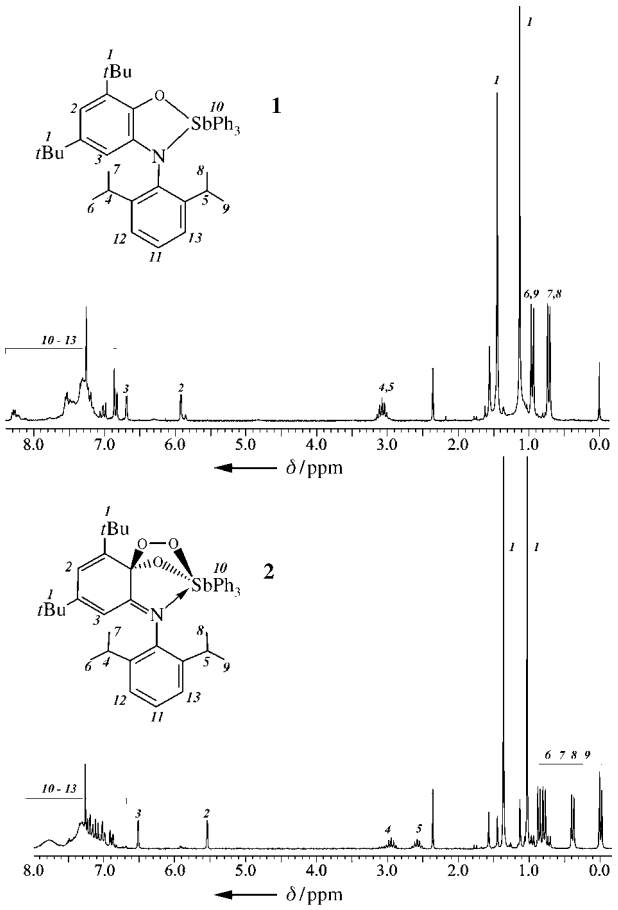


Figure 2. ^{1}H NMR spectra of **1** (top) and **2** (bottom) in $CDCl_3$ at 298 K.

of all proton resonances of **1** decreases, while the intensity of resonances related to **2** increases. Shifts of the signals attributed to the protons of the *tert*-butyl and aromatic groups of a distorted *o*-amidophenolato moiety are observed on addition of dioxygen. In $CDCl_3$, the *tert*-butyl protons of **1** correspond to two singlets at 1.13 and 1.44 ppm, whereas signals from the *tert*-butyl protons of **2** are found at 1.02 and 1.36 ppm. The signals from the aromatic protons in the amidophenolato ligand of **1** appear as doublets centered at 5.91 and 6.69 ppm ($^4J_{H,H} = 2.3$ Hz). The corresponding aro-

matic protons of **2** give rise to doublet signals centered at 5.53 and 6.51 ppm ($^4J_{H,H} = 1.5$ Hz). Furthermore, in contrast to **1** the asymmetry of complex **2** makes the two methine protons and the protons of the four CH_3 groups of the isopropyl substituents at *N*-aryl nonequivalent. Two isopropyl methine protons of **1** appear as a septet centered at 3.07 ppm ($^3J_{H,H} =$ 6.8 Hz). However, the same methine protons in **2** appear as two septets centered at 2.58 and 2.94 ppm ($^3J_{H,H} = 6.8$ Hz). The signals for the isopropyl methyl groups of **1** are two doublets centered at 0.71 and 0.94 ppm ($^3J_{H,H} = 6.8$ Hz), but the same methyl protons of **2** appear as four doublets at −0.02, 0.38, 0.78, and 0.86 ppm ($^3J_{H,H} = 6.8$ Hz).

In the electronic absorption spectra of the reaction mixture, a new band ($\lambda_{max} = 338$ nm) appears while the intensity of the absorption band of **1** ($\lambda_{max} = 300$ nm) decreases.

Complex **1** was completely converted into **2** in [D_6]acetone (2×10^{-3} M) within two hours when the reaction mixture was stirred in air at 290 K. Spiroendoperoxide **2** was isolated from acetone as air-stable, yellow–orange crystals, which contained one solvate acetone molecule per molecule of complex. The molecular structure of **2** was established by single-crystal X-ray analysis (Figure 3). The O(2)–O(3) bridge, which binds the Sb(1) and C(1) atoms, is slightly shorter (1.461(3) Å) than the analogous bond (1.493(5) Å) in a similar Rh complex[7] and close to the O–O bond length in antimony endoperoxide 3,3-dihydro-5,5-dimethyl-3,3,3-triphenyl-1,2,4,3-trioxastibolane (1.468 Å).[8] The Sb(1) atom in **2** has a distorted octahedral coordination environment. The Sb(1)-O(1)-C(1)-C(2) metallacycle of the *o*-amidophenolato ligand is nonplanar. The dihedral angle between the Sb(1)-O(1)-C(1) plane and Sb(1)-N(1)-C(2)-C(1) plane is 125.6°; the O(1)-C(1)-C(2)-N(1) torsion angle is 34.9°. The C(1)–O(1) bond (1.369(4) Å) is typical for a single bond of a phenolate group,[4,5] whereas the C(2)–N(1) interatomic distance (1.287(3) Å) is close to that of a C–N double bond.[4,6] The C(1)–C(2,6) (1.527(4), 1.510(4) Å) bond lengths and angles around C(1) (102.9(2)–115.2(3)°) indicate sp^3 hybridization of the C(1) atom. The Sb–C (2.141(3)–2.144(3) Å) and Sb–O (2.032(2), 2.072(2) Å) bond lengths are typical for Sb^V compounds,[5,9] and the Sb(1)–N(1) separation (2.425(3) Å) is within the range expected for donor–acceptor Sb–N bonds.[6]

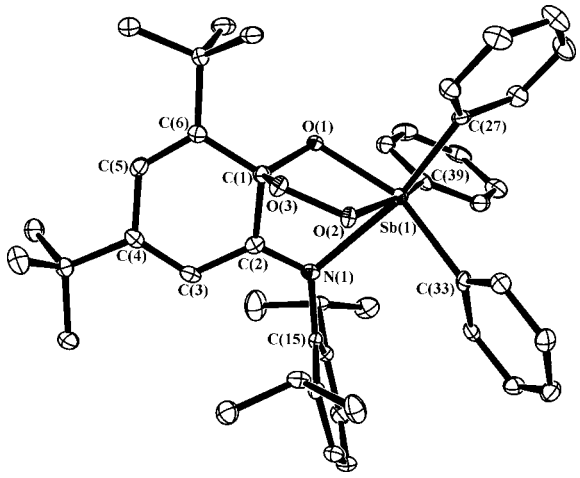


Figure 3. An ORTEP view of **2**, with 30% probability ellipsoids (H atoms are omitted for clariy). Selected bond lengths [Å] and angles [°]: Sb(1)-O(1) 2.032(2), Sb(1)-O(2) 2.072(2), Sb(1)-N(1) 2.425(3), Sb(1)-C(27) 2.141(3), Sb(1)-C(33) 2.144(3), Sb(1)-C(39) 2.144(4), C(1)-O(1) 1.369(4), C(1)-O(3) 1.479(4), N(1)-C(2) 1.287(4), N(1)-C(15) 1.447(4), C(1)-C(2) 1.527(4), C(2)-C(3) 1.433(4), C(3)-C(4) 1.342(5), C(4)-C(5) 1.471(5), C(5)-C(6) 1.347(4), C(1)-C(6) 1.510(4), O(2)-O(3) 1.461(3); N(1)-Sb(1)-O(1) 71.61(8), N(1)-Sb(1)-O(2) 72.77(8), N(1)-Sb(1)-C(27) 163.41(11), O(1)-Sb(1)-C(33) 158.88(10), O(2)-Sb(1)-C(39) 164.80(10), O(1)-Sb(1)-O(2) 79.27(8).

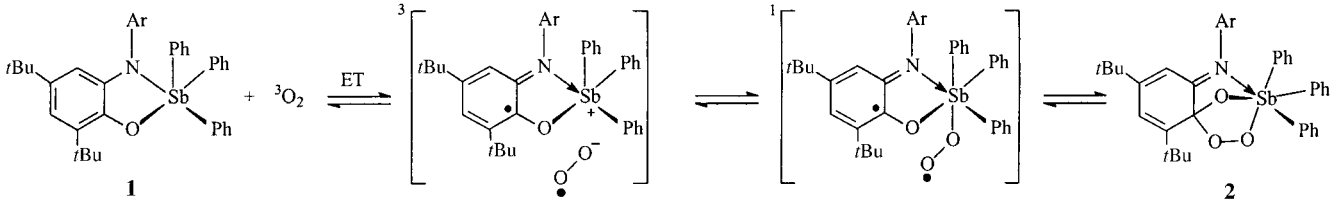
It is remarkable that the transformation of **1** into **2** is completely reversible. Moderate heating of solutions of **2** leads to the initial *o*-amidophenolate **1** by elimination of dioxygen. ^{1}H NMR spectroscopy shows that the conversion of **2** into **1** in [D_6]acetone solution (2×10^{-3} M) is effected by repeating a freeze–pump–warm (50 °C) cycle over 60 minutes. It is necessary to emphasize that **1** reacts with molecular oxygen in its triplet state. The reaction between **1** and O_2 occurs with identical rate under the natural light of the laboratory and in darkness.

Some examples of linear peroxo compounds of antimony are known.[9] The related antimony endoperoxide 3,3-dihydro-5,5-dimethyl-3,3,3-triphenyl-1,2,4,3-trioxastibolane[8] and antimony–oxygen clusters with μ-peroxo ligands have been described previously.[10] However, these compounds are prepared either by exchange reactions or with hydrogen peroxide, but not with dioxygen, and they are not able to eliminate the dioxygen.[8–10]

The unique ability of complex **1** to bind dioxygen reversibly is caused by the redox activity of the *o*-amidophenolate ligand. It is well known that dianions of *o*-aminophenoles, which are similar to catecholate dianions,[11] undergo reversible single-electron oxidation in the coordination sphere of the metal center, which results in the formation of an *o*-iminobenzosemiquinolate.[4,12] Such a transformation can occur by an intramolecular mechanism because of the change in oxidation state of the central atom[12a] or under the influence of an external oxidizer.[4]

We suggest two possible mechanisms for the binding of dioxygen by **1**. The first mechanism assumes a one-electron oxidation of the *o*-amidophenolato ligand by molecular oxygen, with the intermediate formation of an ion pair consisting of the molecular cation $\mathbf{1}^+$ and a superoxide anion (Scheme 3). At the next stage, the triplet diradical complex of antimony(v) that contains the *o*-iminobenzosemiquinonate and peroxo ligands is formed as the result of geminate recombination of ion pairs. Interspin conversion of a triplet state into a singlet state in this diradical is facilitated by the presence of the heavy antimony atom, which has a large spin–orbital interaction constant. The subsequent recombination of the radical centers in the singlet intermediate results in the formation of the final bicyclic endoperoxide **2**. Note that the homolytic substitution reaction on the antimony center with dioxygen takes place even if the electron-transfer stage is omitted. Such a substitution with stable radicals is typical for catecholate complexes.[13]

The second mechanism is similar to that proposed for the reversible binding of triplet dioxygen by bianthrene.[3b] It concerns the formation of a loosely bound complex of **1** and



Scheme 3. Plausible mechanism for the reversible conversion of **1** into **2**. ET = electron transfer.

dioxygen, which then proceeds by a spin-forbidden step with charge transfer from **1** to dioxygen to form **2**. The available data do not allow us to distinguish between these two possible mechanisms. However, we suppose that the first mechanism is more probable. The biradical complex is also the key intermediate in the elimination of molecular oxygen. This biradical complex is formed in the first step by the homolytic splitting of the C–O bond. The essential factor that assists this process is the energy compensation because of the formation of an *o*-iminobenzosemiquinonate chelate ligand bonded to antimony.

Experimental Section

The starting materials used were from commercially available sources (Aldrich, Fluka, Strem) unless otherwise noted. 4,6-Di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)-*o*-iminobenzoquinone was synthesized by using a reported method.[14] Synthetic procedures were carried out under vacuum (for **1**) with dried, distilled solvents. ^{1}H NMR spectra were obtained on a Bruker DPX-200 spectrometer (200 MHz). IR spectra (4000–400 cm^{-1}) were recorded on Specord M-80 in nujol. X-ray data were collected on a Bruker Smart Apex diffractometer.

1: A solution of 4,6-di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)-*o*-iminobenzoquinone (0.76 g, 2 mmol) in toluene (30 mL) was added to a stirred solution of $SbPh_3$ (0.71 g, 2 mmol) in toluene (15 mL). The reaction was allowed to proceed over 3 h at room temperature, during which time the mixture gradually changed color from cherry red to orange. The resulting solution was concentrated to 15 mL and stored for a day at 0°C. The product was isolated by filtration and recrystallized over a longer period from toluene to yield yellow, X-ray-quality crystals (1.39 g, 89%); m.p. 170–171°C; Elemental analysis calcd (%) for $C_{47.5}H_{56}ONSb$ (778.72 g mol^{-1}): C 73.26, H 7.25, Sb 15.63; found: C 72.88, H 6.96, Sb 15.60; IR (Nujol): $\tilde{\nu}$ = 1580w, 1570m, 1450s, 1440s, 1430s, 1415m, 1390s, 1360m, 1330m, 1315w, 1290m, 1240s, 1060s, 1055w, 1025w, 995s, 895w, 865w, 850 m, 825w, 805w, 755w, 730s, 690s, 655m, 605w, 530w, 490w, 455m, 440m cm^{-1}.

^{1}H NMR of **1**·0.5 C_7H_8 (200 MHz, $CDCl_3$, 25°C, TMS): δ = 0.71, 0.94 (both d, $^3J_{H,H}$ = 6.8 Hz, both 6H; 2 CH(CH_3)$_2$), 1.13, 1.44 (both s, both 9H; 2 *t*Bu), 2.36 (s, 0.5 × 3H; CH_3 of toluene), 3.07 (sept, $^3J_{H,H}$ = 6.8 Hz, 2H; 2 CH(CH_3)$_2$), 5.91, 6.69 (both d, $^4J_{H,H}$ = 2.3 Hz, both 1H; C_6H_2 aromatic), 6.8–8.3 ppm (m, 20.5H; 18 protons of aromatic groups in **1** and 0.5 × 5 protons of toluene); ^{1}H NMR of **1**·0.5 C_7H_8 (200 MHz, [D$_6$]acetone, 25°C, TMS): δ = 0.78, 0.96 (both d, $^3J_{H,H}$ = 6.8 Hz, both 6H; 2 CH(CH_3)$_2$), 1.11, 1.42 (both s, both 9H; 2 *t*Bu), 2.32 (s, 0.5 × 3H; CH_3 of toluene), 3.16 (sept, $^3J_{H,H}$ = 6.8 Hz, 2H; 2 CH(CH_3)$_2$), 5.91, 6.70 (both d, $^4J_{H,H}$ = 2.3 Hz, both 1H; C_6H_2 aromatic), 6.9–7.8 ppm (m, 20.5H; 18 protons of aromatic groups in **1** and 0.5 × 5 protons of toluene).

Crystal data for **1**·0.5 C_7H_8: $C_{47.5}H_{56}NOSb$, M_r = 778.72, monoclinic, space group $P2_1/n$, a = 10.525(2), b = 14.861(3), c = 26.426(6) Å; β = 99.855(5)°, V = 4072.5(15) Å^3, Z = 4, ρ_{calcd} = 1.228 g cm^{-3}, T = 293(2) K, F(000) = 1566, λ(Mo$_{K\alpha}$) = 0.71073 Å, μ = 0.710 mm^{-1}. Yellow crystal, 0.50 × 0.04 × 0.04 mm^3, θ = 1.56–23.32°, 27208 reflections collected, 5866 independent reflections (R_{int} = 0.0808); GOF(F^2) = 1.029, R_1(I>2σ(I)) = 0.0455, wR_2 (all data) = 0.0963; largest diff. peak and hole 0.597/−0.350 e Å^{-3}.

2: Compound **1** (195 mg, 0.25 mmol) was dissolved in toluene and left in air for 2 h. The solvent was removed by slow evaporation and the residue was recrystallized from acetone over 3 days to yield yellow–orange crystals of **2**·C_3H_6O suitable for X-ray analysis which were collected and dried in air (144 mg, 80%); m.p. 173–176°C (decomp); IR (nujol): $\tilde{\nu}$ = 1715s, 1645s, 1600m, 1590m, 1570m, 1485s, 1435s, 1365s, 1315w, 1275w, 1260w, 1225s, 1180m, 1140s, 1080m, 1065m, 1030w, 1005w, 985w, 940w, 910m, 870m, 855w, 795 m, 760w, 745s, 730s, 705s, 665w, 625w, 570w, 545w, 535w, 490w, 460s cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$, 25°C, TMS): δ = −0.02 (d, $^3J_{H,H}$ = 6.8 Hz, 3H; CH_3 of *i*Pr), 0.38 (d, $^3J_{H,H}$ = 6.8 Hz, 3H; CH_3 of *i*Pr), 0.78 (d, $^3J_{H,H}$ = 6.8 Hz, 3H; CH_3 of *i*Pr), 0.86 (d, $^3J_{H,H}$ = 6.8 Hz, 3H; CH_3 of *i*Pr); 1.02, 1.36 (both s, both 9H; 2 *t*Bu), 2.58, 2.94 (both sept, $^3J_{H,H}$ = 6.8 Hz, both 1H; 2 CH of 2 *i*Pr), 5.53, 6.51 (both d, $^3J_{H,H}$ = 1.5 Hz, both 1H; C_6H_2 aromatic), 6.8–7.6 ppm (m, 18H; aromatic); ^{1}H NMR (200 MHz, [D$_6$]acetone, 25°C, TMS): δ = 0.01 (d, $^3J_{H,H}$ = 6.8 Hz, 3H; CH_3 of *i*Pr), 0.43 (d, $^3J_{H,H}$ = 6.8 Hz, 3H; CH_3 of *i*Pr), 0.81 (d, $^3J_{H,H}$ = 6.8 Hz, 3H; CH_3 of *i*Pr), 0.88 (d, $^3J_{H,H}$ = 6.8 Hz, 3H; CH_3 of *i*Pr); 1.06, 1.36 (both s, both 9H; 2 *t*Bu), 2.68, 3.03 (both sept, $^3J_{H,H}$ = 6.8 Hz, both 1H; 2 CH of 2 *i*Pr), 5.60, 6.66 (both d, $^4J_{H,H}$ = 1.5 Hz, both 1H; C_6H_2 aromatic), 6.9–8.0 ppm (m, 18H; aromatic).

Crystal data for **2**·C_3H_6O: $C_{47}H_{58}NO_4Sb$, M_r = 822.73, monoclinic, space group $P2_1/n$, a = 13.2049(6), b = 21.8719(10), c = 14.8069(7) Å; β = 97.4860(10)°, V = 4240.0(3) Å^3, Z = 4, ρ_{calcd} = 1.289 g cm^{-3}, T = 100(2) K, F(000) = 1720, λ(Mo$_{K\alpha}$) = 0.71073 Å, μ = 0.693 mm^{-1}; yellow–orange crystal, 0.08 × 0.05 × 0.02 mm^3, θ = 1.67–25.00°, 23334 reflections collected, 7455 independent reflections (R_{int} = 0.0619); GOF(F^2) = 0.970, R_1(I>2σ(I)) = 0.0370, wR_2(all data) = 0.0727; largest diff. peak and hole 0.613/−0.417 e Å^{-3}.

CCDC 253414 (**1**) and 253415 (**2**) 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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