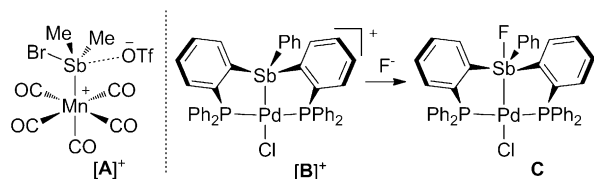


Anion-Controlled Switching of an X Ligand into a Z Ligand: Coordination Non-innocence of a Stiboranyl Ligand**

Iou-Sheng Ke, James S. Jones, and François P. Gabbaï*

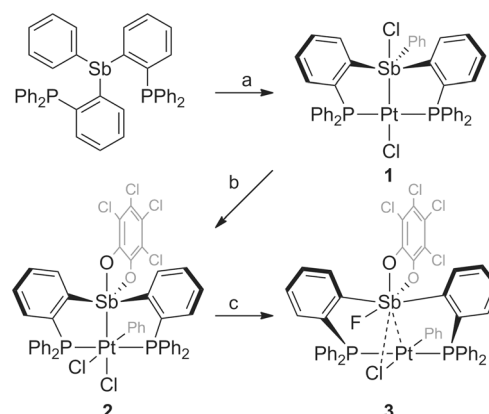
Abstract: The tetravalent platinum stiboranyl complex $[(o-(\text{Ph}_2\text{P})\text{C}_6\text{H}_4)_2(o-\text{C}_6\text{Cl}_4\text{O}_2)\text{Sb}]\text{PtCl}_2\text{Ph}$ (**2**) has been synthesized by reaction of $[(o-(\text{Ph}_2\text{P})\text{C}_6\text{H}_4)_2\text{SbClPh}]\text{PtCl}$ (**1**) with *o*-chloranil. In the presence of fluoride anions, the stiboranyl moiety of **2** displays non-innocent behavior and is readily converted into a fluorostiborane unit. This transformation, which is accompanied by elimination of a chloride ligand from the Pt center, results in the formation of $[(o-(\text{Ph}_2\text{P})\text{C}_6\text{H}_4)_2(o-\text{C}_6\text{Cl}_4\text{O}_2)\text{SbF}]\text{PtClPh}$ (**3**). Structural, spectroscopic, and computational studies show that the conversion of **2** into **3** is accompanied by a cleavage of the covalent Pt–Sb bond present in **2** and formation of a longer and weaker Pt→Sb interaction in **3**. These results show that this new Pt–Sb platform supports the fluoride-induced metamorphosis of a stiboranyl X ligand into a stiborane Z ligand.

The term ligand non-innocence is used when a ligand participates in a redox process which would otherwise be expected to occur at the metal center.^[1] Prototypical examples of systems exhibiting this behavior include metal dithiolene complexes, which undergo successive ligand-based reductions.^[2] Recent results in the coordination chemistry of heavy main-group ligands^[3] suggest that a ligand can also become non-innocent by participating in anion-exchange rather than electron-exchange reactions.^[4] For example, the group of Reid has observed that the antimony atom of the cationic stibine complex $[\text{Mn}(\text{CO})_5(\text{SbMe}_2\text{Br})]^+$ (**[A]**⁺) interacts with an oxygen atom of the



triflate counteranion.^[5] We have also observed that non-halogenated stibines can form strong antimony–anion bonds without dissociation of the antimony–metal interaction.^[4c] Such behavior, which we coin coordination non-innocence, is illustrated by the reaction of the cationic palladium stibine complex **[B]**⁺ which converts into **C** through coordination of a fluoride anion to the antimony rather than the palladium atom.^[4c] Herein we show that the concept of coordination non-innocence can be applied to stiboranyl ligands and exploited for the design of a new anion-responsive platform.^[6] As documented herein, this new platform operates through a fluoride-induced, reversible switching of a stiboranyl X ligand (one-electron donor) into a stiborane Z ligand (σ -accepting ligand).^[7]

Treatment of $[(\text{Et}_2\text{S})_2\text{PtCl}_2]$ with the known bis(phosphanyl)stibine ligand **L**^[4c] proceeded over the course of 12 hours to afford a complex (**1**) characterized by a ³¹P NMR resonance at $\delta = 53.9$ ppm flanked by ¹⁹⁵Pt satellites (¹J_{Pt–P} = 2706 Hz; Scheme 1). The corresponding ¹⁹⁵Pt NMR reso-



Scheme 1. Synthesis of **1**, oxidation of **1** into **2**, and formation of **3**.

a) $[(\text{Et}_2\text{S})_2\text{PtCl}_2]$ CHCl_3 ; b) *o*-chloranil, CHCl_3 ; c) $\text{CHCl}_3/\text{H}_2\text{O}$ (3:1, 0.1 M HCl + 10 equiv KF).

nance appears as a triplet at $\delta = -5019$ ppm. Elucidation of the structure of this complex reveals that the stibine moiety of the ligand is non-innocent, as it undergoes insertion into one of the Pt–Cl bonds.^[8] The Pt–Sb bond [2.5380(8) Å] is slightly longer than that in *cis*- $[\text{PtCl}_2(\text{SbPh}_3)_2]$ (av. 2.50 Å),^[9] a difference which may be assigned to the pentacoordination rather than the tetracoordination of the antimony atom in **1** (Figure 1). Despite the constraints imposed by the rigid ligand backbone, the divalent platinum center adopts the expected square-planar geometry (P1–Pt–P2 = 170.01(6)°, Sb–Pt–Cl1 = 172.36(4)°. The Sb–Cl bond length [2.7532(18) Å] is

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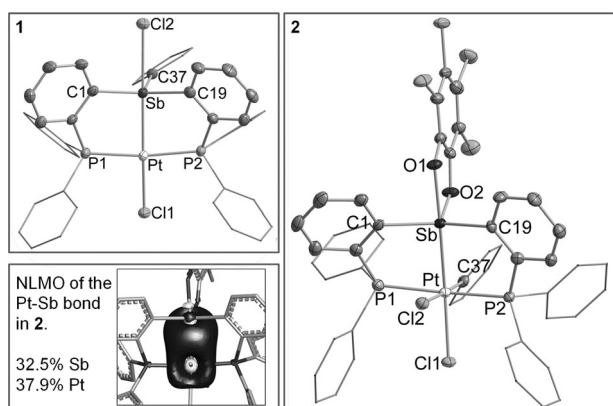


Figure 1. Crystal structures of **1** and **2**. Thermal ellipsoids are drawn at the 50% probability level. Phenyl groups are drawn in wireframe. Hydrogen atoms and solvents are omitted for clarity. Selected bond lengths [Å] and angles [°]: **1**: Sb–Pt 2.5380(8), Pt–Cl1 2.3851(16), Sb–Cl2 2.7532(18); P1–Pt–P2 170.01(6), Sb–Pt–Cl1 172.36(4), C1–Sb–C19 124.2(2), C1–Sb–C37 122.3(2), C19–Sb–C37 108.6(2). **2**: Sb–Pt 2.5906(5), Pt–Cl1 2.4235(11), Pt–Cl2 2.4608(12), Sb–O1 2.1239(3), Sb–O2 2.002(3); P1–Pt–P2 170.71(4), Cl2–Pt–C37 177.99(13), Sb–Pt–Cl1 167.77(3), O1–Sb–Pt 176.12(8), C1–Sb–C19 133.47(17), C19–Sb–O2 110.84(16), O2–Sb–Cl1 111.02(16). Bottom left: NLMO plot (isodensity value = 0.05) of the Sb–Pt bond in **2** obtained from NBO analysis. Hydrogen atoms are omitted for clarity.

comparable that in Ph_4SbCl [2.740(6) Å].^[10] Compound **1** is air stable and does not decompose in wet organic solutions. It is, however, sensitive to oxidants and quickly reacts with *o*-chloranil (*o*- $\text{O}_2\text{C}_6\text{Cl}_4$), a compound known to convert stibines into the corresponding tetrachlorocatecholate stiboranes. This reaction proceeds cleanly in CHCl_3 to afford the complex **2** as a yellow, air-stable solid. The ^{31}P NMR spectrum of **2** in CDCl_3 shows a signal at $\delta = 45.51$ ppm ($^1J_{\text{Pt-P}} = 2192$ Hz), thus indicating that the phosphines remain coordinated to the platinum center. The ^{195}Pt NMR resonance of **2** at $\delta = -3742$ ppm is significantly upfield from that of **1**, thus suggesting an increase in the valence of the metal center.^[11] Also, when compared to **1** ($^1J_{\text{Pt-P}} = 2706$ Hz), the $J_{\text{Pt-P}}$ value of **2** appears to be notably reduced, a phenomenon that is commonly observed for phosphine platinum complexes upon oxidation.^[11b,12] A final elucidation of the structure of this complex was derived from an X-ray diffraction study^[8] which reveals that the oxidation reaction induces a migration of a chloride and a phenyl ligand from antimony to platinum concomitant with the coordination of the tetrachlorocatecholate ligand at the antimony center. As a result of this ligand redistribution reaction, the platinum center adopts an octahedral geometry characteristic of the tetravalent state, while the antimony remains trigonal bipyramidal as in **1**. These changes are accompanied by a slight elongation of the Pt–Sb bond from 2.5380(8) Å in **1** to 2.5906(5) Å in **2**, which can be assigned to the higher coordination number of the platinum atom.

With this new compound in hand, we decided to test its reactivity toward fluoride anions under biphasic conditions. Although hydrolysis occurs with unbuffered water (Millipore purified, pH 5), solutions of **2** in CH_2Cl_2 are stable when layered with acidified water (0.1M HCl). Interestingly, upon

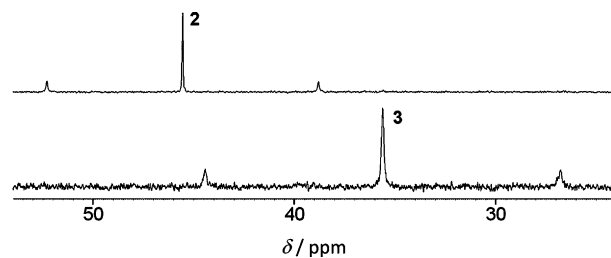


Figure 2. ^{31}P NMR spectra showing the conversion of **2** into **3**. The spectra shown were obtained by layering and briefly (5 s) shaking a CHCl_3 solution of **2** (9.3×10^{-3} M, 0.6 mL) with a KF solution obtained by adding KF (3.3 mg) to an HCl solution (0.1 M, 0.2 mL).

addition of KF (10 equiv) to the acidified water layer, **2** is readily converted into a new species (**3**) featuring a ^{31}P NMR resonance at $\delta = 35.5$ ppm (Figure 2) with a coupling constant $^1J_{\text{Pt-P}}$ of 2855 Hz. This coupling constant is significantly larger than that of **2** ($^1J_{\text{Pt-P}} = 2192$ Hz), thus signaling increased density at the platinum center. Formation of a Sb–F bond is supported by a ^{19}F NMR resonance at $\delta = -77.1$ ppm which is close to the chemical shift measured for Ph_4SbF ($\delta = -81.4$ ppm).^[13] The ^1H NMR spectrum of this complex indicates that the organic phenyl and *o*-phenylene diphenylphosphine ligands present in **2** are retained in **3**. The conversion of **2** into **3** can be reversed by addition of a fluoride scavenger such as AlCl_3 to the aqueous layer. Compound **3**, which can also be prepared by reaction of **2** with KF in methanol/ CH_2Cl_2 , shows no sign of kinetic instability when dissolved in CHCl_3 and heated to 50 °C.

To rationalize the above spectroscopic changes, a single crystal of **3** was subjected to an X-ray diffraction study. This structural assay indicates some drastic structural changes at the core of the complex. In terms of composition, **2** and **3** only differ by the nature of one of the halide ligands. While **2** had two platinum-bound chloride anions, the structure of **3** shows that only one of these chloride anions remains.^[8] The second chloride is replaced by a fluoride anion, which is bound to the antimony atom [Sb–F = 1.957(7) Å].^[13] As a result of this new substitution pattern the Sb–Pt covalent bond of **2** is no longer present in **3**, which instead features a divalent square-planar platinum center positioned over the open face of an acidic, square-pyramidal fluorostiborane unit.^[14] This structural arrangement, along with the Pt···Sb separation of 3.0868(11) Å is consistent with the presence of a Pt→Sb interaction, thus implying that the fluorostiborane unit is acting as a Z ligand. We also note that the ^{195}Pt NMR resonance of **3** at $\delta = -3714$ ppm is significantly downfield from that reported for complexes such as *trans*-(*p*- MeOC_6H_4) $\text{PtCl}(\text{PPh}_3)_2$ [$\delta(^{195}\text{Pt}) = -4365$ ppm].^[15] This downfield shift is also consistent with transfer of density from platinum to antimony, a phenomenon analogous to that proposed for a series of complexes of general formula $\text{NCN}(\text{X})\text{Pt} \rightarrow \text{SO}_2$ (NCN = 2,6-[(Me_2N) CH_2] $_2\text{C}_6\text{H}_4$ and X = halide).^[16] This Lewis-acidic fluorostiborane is also engaged in a weak Pt–Cl→Sb interaction of 2.831(3) Å. This Sb–Cl distance is much longer than that in related antimonate structures such as [(*o*- $\text{O}(\text{CF}_3)_2\text{C}_6\text{H}_4$) $_2\text{SbCl}_2$][NBu_4] (avg. 2.450(1) Å),^[17] and is in line with the secondary nature of the Cl→Sb interaction. We also note

that the Pt–Cl distance of 2.432(3) Å is similar to that found in *trans* [Pt(PPh₃)₂PhCl] (2.408(5) Å),^[18] thus indicating tight coordination of the chloride ligand to platinum rather than antimony.

DFT calculations (Gaussian 09 program, functional: BP86 mixed basis sets: Sb/Pt, VTZ-PP cc-pVTZ-PP; P/Cl, 6-311 + g(d); C/H, 6-31g) and subsequent natural bond orbital (NBO) analyses support the notion that the stiboranyl X ligand of **2** switches into a stiborane Z ligand in **3**. Indeed, the NBO analysis treats the Sb–Pt bond of **2** as a σ bond, which as indicated by the atomic contributions (32.5% for Sb and 37.9% for Pt) is highly covalent (Figure 1). The NBO analysis of **3** projects a very different picture with the two atoms now interacting through second-order d(Pt)→ σ^* (Sb) donor–acceptor interactions (Figure 3). The delocalization energies

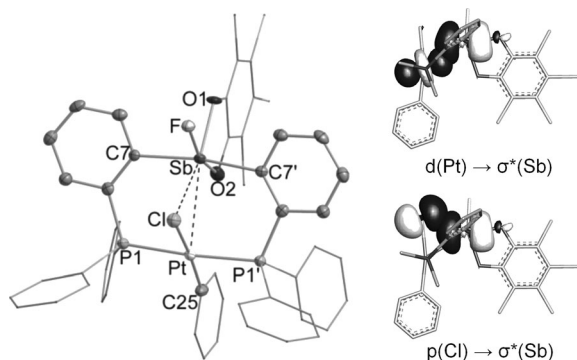


Figure 3. Left: Structure of **3**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sb–F 1.957(7), Sb–Cl 2.831(3), Pt–Cl 2.432(3), Sb–O1 2.031(8), Sb–O2 2.093(10), P1–Pt–P1' 172.21(11), Cl–Pt–C25 173.7(4), Pt–Sb–O1 154.8(3), Cl–Sb–O1 156.9(3), F–Sb–O2 160.9(3), C7–Sb–C7' 168.2(4), Sb–Cl–Pt 71.35(9), O1–Sb–O2 80.4(4), F–Sb–Cl 76.5(2). Right: NBO plots (isodensity value = 0.05) of the main Pt→Sb and Cl→Sb interactions in **3**. Hydrogen atoms are omitted and some phenyl groups are truncated for clarity.

of these d(Pt)→ σ^* (Sb) add up to 59.9 kcal mol^{−1}. Finally, this NBO treatment shows that the long Sb–Cl contact is also associated with donor–acceptor interactions [p(Cl)→ σ^* (Sb)] whose combined delocalization energy equals 26.2 kcal mol^{−1}. These computational results suggest that in **2**, the antimony moiety acts as an X-type stiboranyl ligand. In **3**, however, coordination of fluoride to antimony triggers a cleavage of the Sb–Pt bond to produce a stiborane moiety, which acts as a Z-type ligand towards the platinum center and a Lewis acid towards the proximal chloride.

This anion-induced change of the antimony ligand observed on going from **2** to **3** is also accompanied by the appearance of a dark-orange color. UV/Vis monitoring indicates that this color change is associated with the appearance of low-energy bands which extend into the visible range of the spectrum. TD-DFT calculations carried out with the MPW1PW91 functional show that these spectral changes are caused by a series of low-energy transitions. The three low-energy transitions of highest intensity (labeled as A–C in Figure 4) share the common feature of having the LUMO as

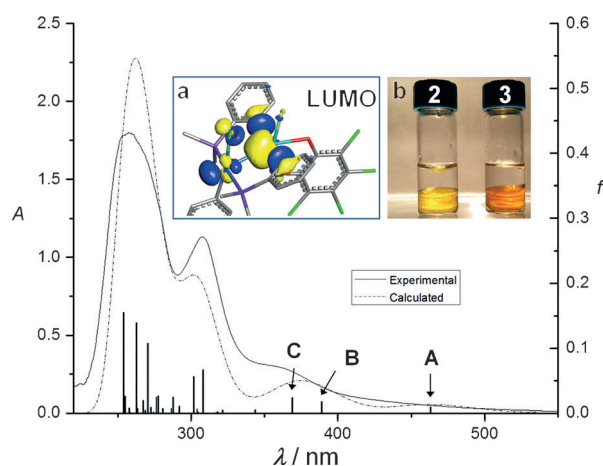


Figure 4. Experimental and calculated (TD-DFT) UV/visible spectrum of **3** with the computed excitations shown as thin lines with heights proportional to the calculated oscillator strengths. Inset (a) shows the LUMO of **3**. Inset (b) shows the color change observed upon conversion of **2** into **3**.

the sole accepting orbital. Examination of the LUMO shows that it possesses a large lobe of σ^* (Sb–O) character located on the antimony. The make-up of this LUMO and its large antimony character is a direct consequence of the cleavage of the Sb–Pt bond, which generates coordinative unsaturation at the antimony center.

In conclusion, we report a new fluoride anion-responsive platform whose properties originate from the coordination non-innocence of an antimony ligand. Fluoride coordination to this platform triggers a reversible switch of a stiboranyl X ligand (one-electron donor) into a stiborane Z ligand (σ -accepting ligand). We are currently working to exploit such a switching behavior for the design of new anion sensors and anion-actuated molecular devices.

Experimental Section

(*o*-(Ph₃P)C₆H₄)₂PhSb (**L**)^[4c] and cis-PtCl₂(Et₂S)₂^[19] were prepared according to the reported procedures. Solvents were dried by passing through an alumina column (*n*-pentane and CH₂Cl₂) or by reflux under N₂ over Na/K (Et₂O and THF). All other solvents were used as received. SbCl₃ and *o*-chloranil were purchased from Aldrich and used as received. All air- and moisture-sensitive manipulations were carried out under an atmosphere of dry N₂ employing either a glove box or standard Schlenk techniques. Ambient-temperature NMR spectra were recorded on a Varian Inova 500 FT NMR (499.43 MHz for ¹H, 125.58 MHz for ¹³C) spectrometer or a Varian Unity Inova 400 FT NMR (399.59 MHz for ¹H, 100.45 MHz for ¹³C, 85.69 for ¹⁹⁵Pt, 375.99 MHz for ¹⁹F, 161.74 MHz for ³¹P) spectrometer. Chemical shifts (δ) are given in ppm and are referenced against residual solvent signals (¹H, ¹³C) or external BF₃·Et₂O (¹⁹F), H₃PO₄ (³¹P), K₂PtCl₄ in D₂O (¹⁹⁵Pt). Elemental analyses were performed at Atlantic Microlab (Norcross, GA).

Synthesis of 1: A solution of [(Et₂S)₂PtCl₂] (62 mg, 0.14 mmol) in CH₂Cl₂ (2 mL) was added to a solution of **L** (100 mg, 0.14 mmol) in CH₂Cl₂ (10 mL) and the resulting yellow solution was allowed to stir for 12 h at room temperature. The reaction mixture was concentrated to about 2 mL, and the product precipitated by addition of *n*-pentane (10 mL). The product was filtered and washed with *n*-pentane (3 ×

5 mL) to afford **1** (112 mg, 82%) as a yellow solid. Single crystals of **1** suitable for X-ray diffraction were obtained by vapor diffusion of Et₂O into a solution of the compound in CH₂Cl₂. ¹H NMR (499.43 MHz; CDCl₃): δ = 6.68 (t, 2H, *o*-P(Sb)C₆H₄, ³J_{H-H} = 9.50 Hz), 6.78 (d, 2H, *o*-P(Sb)C₆H₄, ³J_{H-H} = 9.50 Hz), 6.90 (t, 1H, SbPh-CH, ³J_{H-H} = 9.00 Hz), 7.29–7.33 (m, 6H, PPh-CH), 7.37–7.56 (m, 18H, PPh-CH + SbPh-CH), 7.80 (t, 2H, *o*-P(Sb)C₆H₄, ³J_{H-H} = 9.50 Hz), 9.92 ppm (d, 2H, *o*-P(Sb)C₆H₄, ³J_{H-H} = 9.50 Hz). ¹³C{¹H} NMR (125.58 MHz; CDCl₃): δ = 128.58 (s), 129.20 (t, J_{C-P} = 6.66 Hz), 129.65 (s), 131.61 (s), 132.08 (s), 133.15 (s), 133.51 (s), 133.77 (s), 133.85 (s), 133.91 (s), 133.97–134.10 (bm, 2C), 135.21 (s), 139.51 ppm (t, J_{C-P} = 9.54 Hz). ³¹P{¹H} NMR (161.74 MHz; CDCl₃): δ = 53.95 ppm (s, ¹J_{P-195Pt} = 2706 Hz). ¹⁹⁵P{¹H} NMR (85.69 MHz; CDCl₃): δ = –5016 ppm (t, ¹J_{P-195Pt} = 2706 Hz). C,H analysis calculated (%) for C₄₂H₃₃Cl₂P₂PtSb·0.5CH₂Cl₂: C 49.57, H 3.33; found C 49.25, H 3.42.

Synthesis of **2**: A solution of *o*-chloranil (32 mg, 0.13 mmol) in CHCl₃ (2 mL) was added dropwise to a solution of **1** (130 mg, 0.13 mmol) in CHCl₃ (2 mL) at room temperature. The resulting orange solution was allowed to stir for 12 h before adding *n*-pentane (10 mL) upon which a yellow precipitate was formed. The solid was filtered, washed with *n*-pentane (3 × 3 mL), and dried under vacuum to afford 99 mg (62%) of **2**. Single crystals of **2** suitable for X-ray diffraction were obtained by slow diffusion of Et₂O into a solution of the compound in THF. ¹H NMR (499.43 MHz; CDCl₃): δ = 5.96 (t, 1H, SbPh-CH, ³J_{H-H} = 7.00 Hz), 6.46 (d, 2H, *o*-P(Sb)C₆H₄, ³J_{H-H} = 8.50 Hz), 6.53 (t, 1H, SbPh-CH, ³J_{H-H} = 7.00 Hz), 6.75 (d, 1H, SbPh-CH, ³J_{H-H} = 7.00 Hz), 6.94–6.97 (m, 2H, SbPh-CH), 7.10–7.12 (m, 2H, *o*-P(Sb)C₆H₄), 7.17 (t, 4H, PPh-CH, ³J_{H-H} = 7.00 Hz), 7.37–7.48 (m, 12H, PPh-CH), 7.62–7.68 (m, 4H, PPh-CH), 7.78–7.82 (m, 2H, *o*-P(Sb)C₆H₄), 8.94 ppm (d, 2H, *o*-P(Sb)C₆H₄, ³J_{H-H} = 8.50 Hz). ¹³C NMR (125.58 MHz; CDCl₃): δ = 116.75 (s, O₂C₆Cl₄), 120.23 (s, O₂C₆Cl₄), 123.67 (s, O₂C₆Cl₄), 125.54 (s, O₂C₆Cl₄), 125.76 (s), 126.01 (s), 126.24 (s), 126.50 (s), 126.61 (s), 126.97 (s), 127.65 (t, J_{C-P} = 5.40 Hz), 128.06 (t, J_{C-P} = 5.40 Hz), 130.77 (s), 131.75 (s), 132.31 (s), 133.69 (t, J_{C-P} = 5.27 Hz), 135.94 (t, J_{C-P} = 5.27 Hz), 136.32 (m), 136.55 (m), 143.02 (s, O₂C₆Cl₄), 145.87 (s, O₂C₆Cl₄), 153.17 ppm (t, *o*-P(Sb)C₆H₄, ³J_{C-P} = 17.83 Hz). ³¹P{¹H} NMR (161.74 MHz; CDCl₃): δ = 45.51 ppm (s, ¹J_{P-195Pt} = 2192 Hz). ¹⁹⁵P{¹H} NMR (85.69 MHz; CDCl₃): δ = –3740 ppm (t, ¹J_{P-195Pt} = 2192 Hz). C,H analysis calculated (%) for C₄₈H₃₃Cl₆O₂P₂PtSb: C 46.75, H 2.70; found C 47.01, H 2.71.

Synthesis of **3**: A solution of KF (4 mg, 0.06 mmol) in 0.5 mL MeOH was added to a stirred, yellow suspension of **2** (77 mg, 0.06 mmol) in 2 mL CH₂Cl₂. After stirring for 1 h, all volatiles were removed from the resulting orange suspension to give an orange solid, which was extracted with 6 mL cold CH₂Cl₂. The resulting orange solution was filtered over a plug of Celite, after which all volatiles were removed to yield 55 mg (73%) of **3** as an orange-red powder. Single crystals suitable for X-ray diffraction were obtained by layering a CH₂Cl₂ solution of the compound with *n*-pentane. ¹H NMR (399.59 MHz; CDCl₃): δ = 6.11 (s, 1H, SbPh-CH), 6.35–6.49 (m, 2H, SbPh-CH), 6.49–6.59 (m, 3H, SbPh-CH), 6.87 (t, 4H, PPh-CH, ³J_{H-H} = 7.30 Hz), 7.11 (t, 2H, *o*-P(Sb)C₆H₄, ³J_{H-H} = 6.80 Hz), 7.15–7.43 (m, 8H, PPh-CH), 7.46–7.62 (m, 8H, PPh-CH), 7.97–8.10 (m, 4H, *o*-P(Sb)C₆H₄), 8.44 ppm (d, 2H, *o*-P(Sb)C₆H₄, ³J_{H-H} = 7.77 Hz). ¹³C NMR (100.45 MHz; CDCl₃): δ = 122.94 (s), 126.40 (s), 126.79 (s), 127.54 (s), 127.76 (t, J_{C-P} = 5.02 Hz), 128.01 (s), 128.82 (s), 129.00 (t, J_{C-P} = 5.53 Hz), 129.34 (s), 129.89 (s), 132.28 (s), 132.63 (s), 132.86 (t, J_{C-P} = 4.62 Hz), 133.15 (dt, J_{C-P} = 7.11, 2.49 Hz), 135.39 (t, J_{C-P} = 6.03 Hz), 136.04 ppm (s). Resonances corresponding to the *o*-tetrachlorocatecholate moiety were not observed. ¹⁹F{¹H} NMR (375.99 MHz; CDCl₃): δ = –77.12 ppm (br. s). ³¹P{¹H} NMR (161.74 MHz; CDCl₃): δ = 35.50 ppm (s, ¹J_{P-195Pt} = 2855 Hz). ¹⁹⁵P{¹H} NMR (85.69 MHz; CDCl₃): δ = –3712 ppm (t, ¹J_{P-195Pt} =

2855 Hz). C,H analysis calculated (%) for C₄₈H₃₃Cl₅FO₂P₂PtSb: C 47.38, H 2.73; found C 46.86, H 2.89.

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