

Supporting Information

Coordination of a stibine oxide to a Lewis acidic stiborane at the upper rim of the biphenylene backbone

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Figure S1. ^1H NMR spectrum of 2 in CDCl_3 at room temperature.	5
Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2 in CDCl_3 at room temperature.	5
Figure S1. ^1H NMR spectrum of 3 in CDCl_3 at room temperature.	6
Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 3 in CDCl_3 at room temperature.	6
 Table S1. Crystal data, data collection, and structure refinement for 2	 7
Table S2. Crystal data, data collection, and structure refinement for 3 -(CHCl_3) ₂	8
Table S3. XYZ coordinate of the optimized structure of 3	9

Experimental section.

General Methods. *n*Butyllithium (2.65 M in hexane), antimony trichloride (SbCl₃) and triphenyl stibine (Ph₃Sb) were purchased from Alfa Aesar and used without further purification. Ph₂SbCl was obtained by directly reacting SbCl₃ (1 equiv) with Ph₃Sb (2 equiv) at room temperature under nitrogen for 3 days. The resulting solid was purified by recrystallization in CH₂Cl₂ at -30 °C. Tetrachloro-*o*-benzoquinone (*o*-chloranil) was purchased from Acros Organics and used without further purification. **1**, 8-Dibromobiphenylene and compound **1** were prepared by following the literature procedures.¹ All preparations were carried out under a dry N₂ atmosphere employing either a glovebox or standard Schlenk techniques. Solvents were dried by passing through an alumina column (*n*-pentane and CH₂Cl₂) or by refluxing under N₂ over Na/K (Et₂O and THF). All other solvents were ACS reagent grade and used as received. NMR spectra were recorded on an Inova 500 FT NMR (499.41 MHz for ¹H) spectrometer, Varian NMRS 500RM NMR spectrometer (499.69 MHz for ¹H) or an Inova 400 FT NMR (399.46 MHz for ¹H) spectrometer at room temperature. Chemical shifts are given in ppm and are referenced to residual ¹H or ¹³C solvent signals. Elemental analyses were performed by Atlantic Microlab (Norcross, GA).

Computational details. Density functional theory (DFT) structural optimizations were done with the *Gaussian 09* program. In all cases, the structures were optimized using the B3LYP functional and the following mixed basis set: Sb, cc-pVTZ-PP/ECP28; F, 6-31g(d'); C/O/H, 6-31g; Cl, 6-311g(d). For all optimized structures, frequency calculations were carried out to confirm the absence of imaginary frequencies. The molecular orbitals were visualized and plotted using the *Jimp2* program. The NBO analysis was performed using the NBO 5.9 program. The energy of the Sb=O→Sb interaction was derived from an NBO deletion calculation in which the Kohn Sham elements corresponding to the O→Sb interaction were eliminated.

Crystallographic details. The crystallographic measurements were performed at 110(2) K using a Bruker APEX-II CCD area detector diffractometer, with a graphite-monochromated Mo-K α radiation (λ = 0.71073 Å). A specimen of suitable size and quality was selected and mounted onto a nylon loop. The semi-empirical method SADABS was applied for absorption correction. The structure was solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinement on *F*² using the SHELXTL/PC package (version 6.1) and Olex² allowed location of the remaining non-hydrogen atoms. All H-atoms were geometrically placed and refined using a standard riding model.

Synthesis of 2. A suspension of **1** (500 mg, 1.05 mmol) and Ph₂SbCl (2 g, 6.4 mmol) in toluene (15 ml) was refluxed in a sealed Schlenk tube for 24 h. After cooling to room temperature, the solvent was removed under vacuum. The resulting brown solid was first washed with MeOH (20 ml) and then hexanes (20 ml) to afford **2** as a pale-yellow solid in 22 % yield. ¹H NMR (499.46 MHz, 25 °C, CDCl₃): δ 7.38-7.37 (m, 8 H, Sb-Ph), 7.29-7.27 (m, 12 H, Sb-Ph), 6.63-6.58 (m, 4 H, biphenylene-CH), 6.49 (d, 2 H, ³J_{H-H} = 7.8 Hz,) ppm. ¹³C NMR (125.61 MHz, 25 °C, CDCl₃): δ 160.8, 151.5, 138.3, 136.3, 135.0, 128.8, 128.8, 128.4, 128.3, 116.9 ppm. Elemental analysis: calculated (%) for C₃₆H₂₆Sb₂: C, 61.58; H, 3.73; found C, 61.11; H, 3.83.

Synthesis of 3. A solution of *o*-chloranil (92 mg, 0.38 mmol, 2 equiv) in CH₂Cl₂ (3 mL) was slowly transferred via cannula into a flask containing a solution of **2** (150 mg, 0.19 mmol, 1 equiv) in CH₂Cl₂ (5 mL) in an open flask at room temperature. The oxidation of the distibine resulted in the disappearance of the bright red colour of *o*-chloranil. After stirring for 2 h at room temperature, the solvent was removed under vacuum. The resulting yellow solid was washed by MeOH (20 mL) twice to afford **3** as a yellow solid in 61 % yield. ¹H NMR (499.47 MHz, CDCl₃): δ 7.81 (d, 4 H, ³J_{H-H} = 6.8 Hz, Sb-Ph), 7.49-7.44 (m, 6 H, Sb-Ph), 7.34 (d, 4 H,

$^3J_{\text{H-H}} = 6.8$ Hz, Sb-*Ph*), 7.24 (d, 2 H, Sb-*Ph*), 7.17 (t, 4 H, $^3J_{\text{H-H}} = 7.8$ Hz, Sb-*Ph*), 6.84 (dd, 2 H, $^3J_{\text{H-H}} = 6.8$ Hz, $^4J_{\text{H-H}} = 1.0$ Hz biphenylene-CH), 6.80 (pseudo t, 2 H, $^3J_{\text{H-H}} = 6.8$ Hz, biphenylene-CH), 6.70 (d, 2 H, $^3J_{\text{H-H}} = 7.3$ Hz, biphenylene-CH) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.60 MHz, CDCl_3): δ 152.7, 147.7, 145.2, 134.9, 134.1, 134.0, 133.8, 133.5, 133.0, 132.2, 131.0, 130.7, 130.6, 129.9, 129.7, 129.7, 129.4, 129.3, 128.7, 128.6, 119.6, 119.6, 119.2, 118.6, 117.7, 117.5, 116.9 ppm. High Resolution Mass Spectrometry: calculated for $[\text{C}_{42}\text{H}_{27}\text{Cl}_4\text{O}_3\text{Sb}_2]^+$ ($[\text{M}+\text{H}]^+$) 964.8760; found 964.8835. The purity of this compound was assessed by NMR spectroscopy.

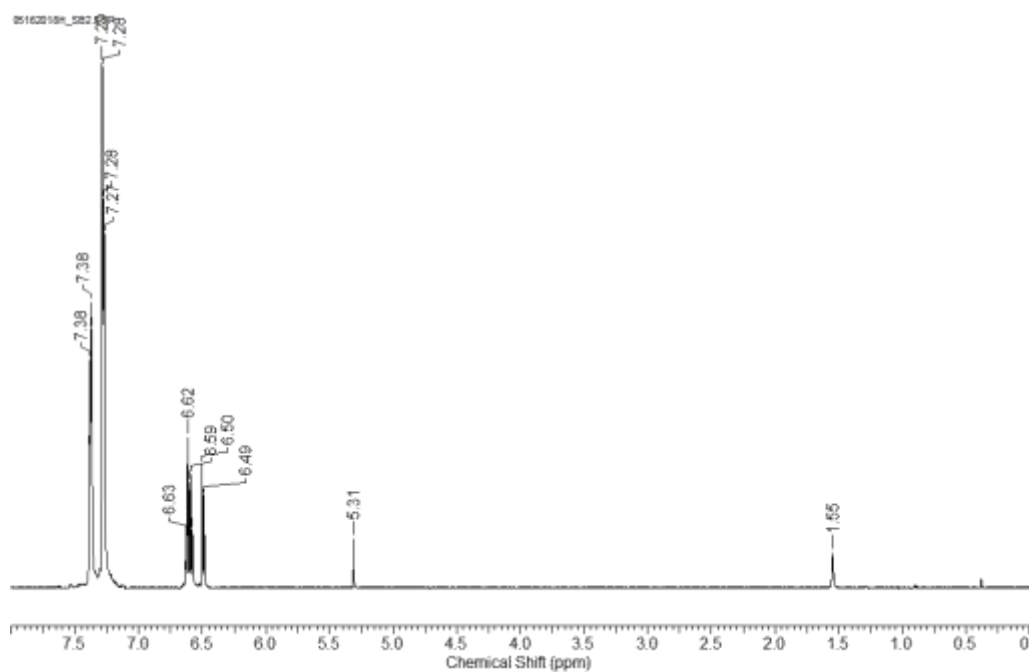


Figure S1. ¹H NMR spectrum of **2** in CDCl₃ at room temperature.

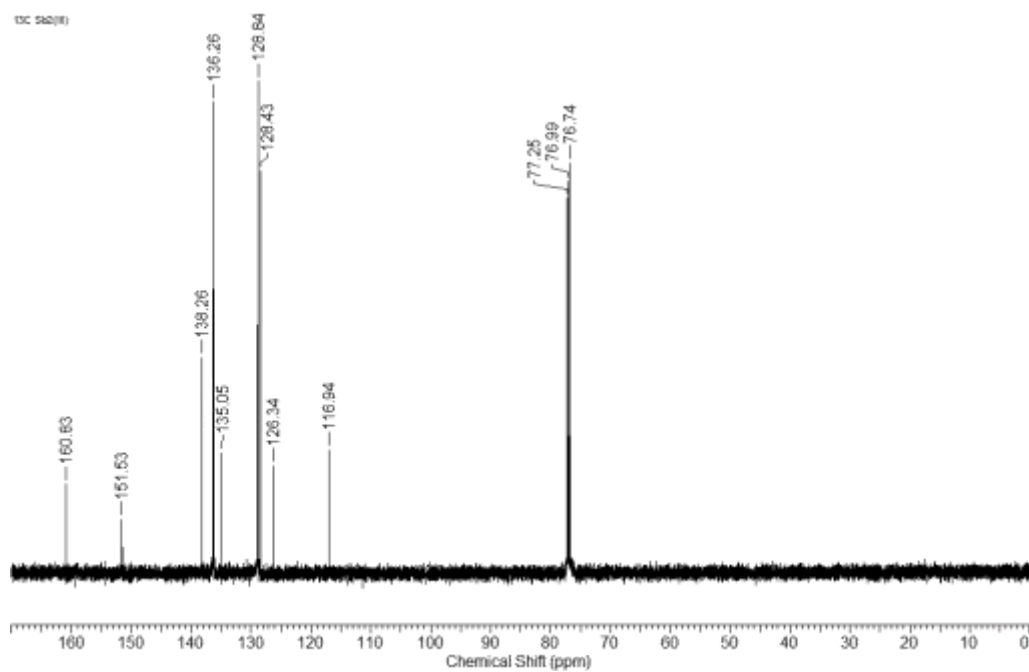


Figure S2. ¹³C{¹H} NMR spectrum of **2** in CDCl₃ at room temperature.

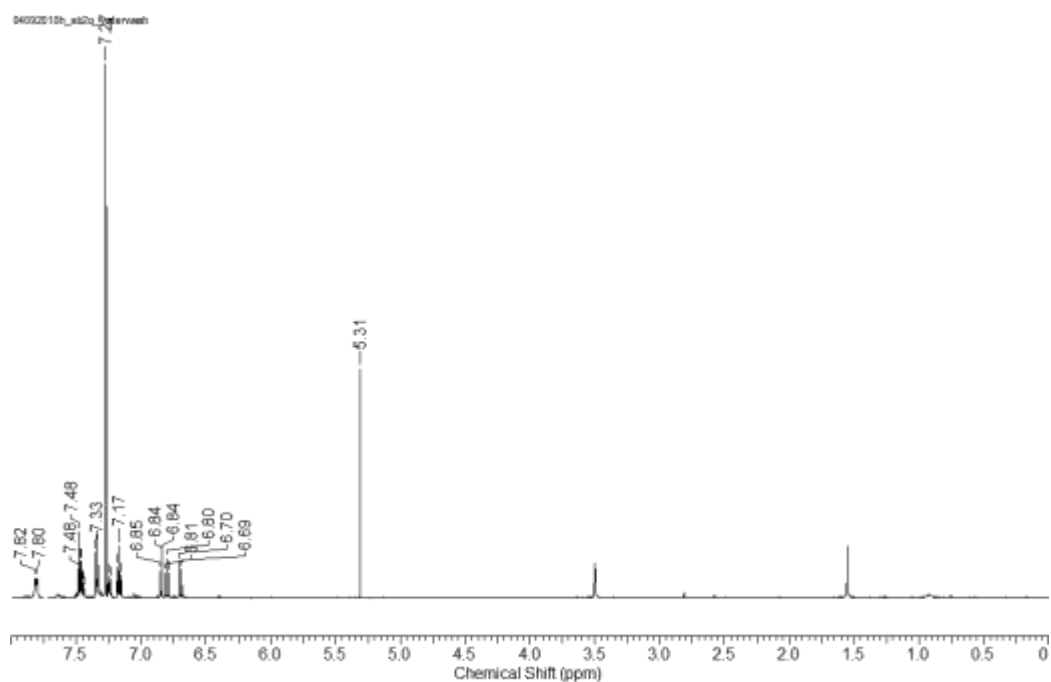


Figure S3. ¹H NMR spectrum of **3** in CDCl₃ at room temperature.

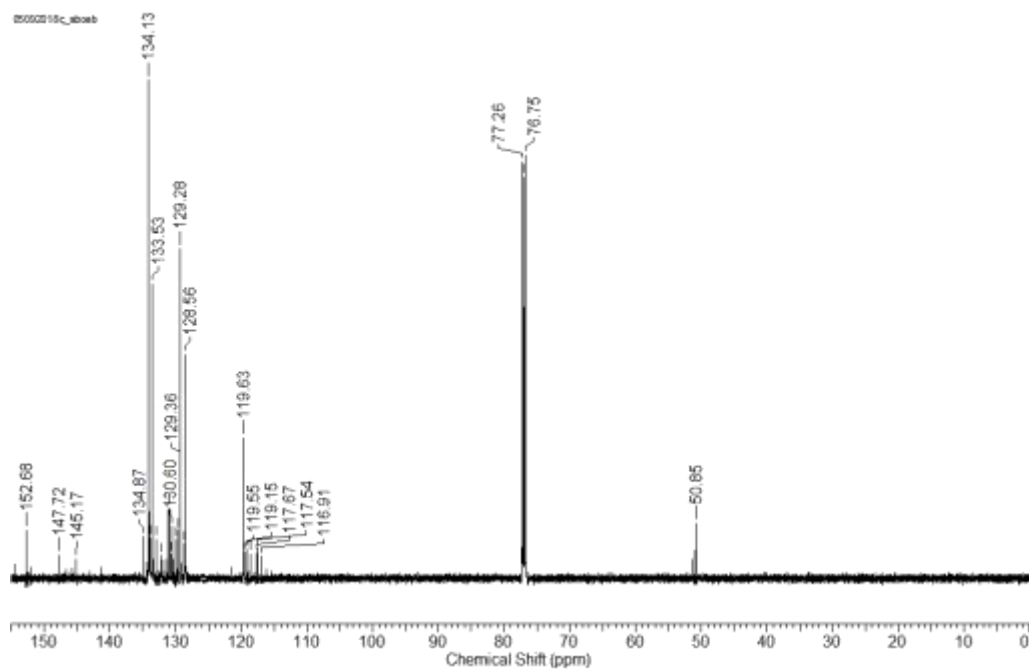


Figure S4. ¹³C{¹H} NMR spectrum of **3** in CDCl₃ at room temperature.

Table S1. Crystal data, data collection, and structure refinement for **2**.

Identification code	y
Empirical formula	C ₃₆ H ₂₆ Sb ₂
Formula weight	702.07
Temperature	110 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>P</i> 1 2 ₁ 1
Unit cell dimensions	a = 6.205(3) Å b = 17.811(9) Å c = 12.643(6) Å $\alpha = 90^\circ$. $\beta = 96.512(6)^\circ$. $\gamma = 90^\circ$.
Volume	1388.2(12) Å ³
Z	2
Density (calculated)	1.680 Mg/m ³
Absorption coefficient	1.969 mm ⁻¹
F(000)	688
Crystal size	0.18 x 0.05 x 0.04 mm ³
Theta range for data collection	1.621 to 26.782°.
Index ranges	-7 ≤ h ≤ 7, -22 ≤ k ≤ 22, -14 ≤ l ≤ 15
Reflections collected	13087
Independent reflections	5877 [R(int) = 0.0630]
Completeness to theta = 25.242°	100.00%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7454 and 0.5998
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5877 / 1 / 343
Goodness-of-fit on F ²	0.997
Final R indices [I > 2σ(I)]	R1 = 0.0433, wR2 = 0.0946
R indices (all data)	R1 = 0.0511, wR2 = 0.0986
Absolute structure parameter	0.05(3)
Largest diff. peak and hole	0.705 and -1.619 e.Å ⁻³

Table S2. Crystal data, data collection, and structure refinement for **3**-(CHCl₃)_{1.43}.

Identification code	y
Empirical formula	C ₄₂ H ₂₆ Cl ₄ O ₃ Sb ₂ , 1.43(CHCl ₃)
Formula weight	1134.83
Temperature	110 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P12 ₁ /c1
Unit cell dimensions	a = 16.192(2) Å b = 17.205(3) Å c = 16.316(2) Å $\alpha = 90^\circ$. $\beta = 90.4177(19)^\circ$. $\gamma = 90^\circ$.
Volume	4545.0(12) Å ³
Z	4
Density (calculated)	1.658 Mg/m ³
Absorption coefficient	1.714 mm ⁻¹
F(000)	2220
Crystal size	0.15 x 0.06 x 0.05 mm ³
Theta range for data collection	1.720 to 26.449°.
Index ranges	-20 ≤ h ≤ 20, -21 ≤ k ≤ 21, -20 ≤ l ≤ 20
Reflections collected	49072
Independent reflections	9353 [R(int) = 0.0878]
Completeness to theta = 25.242°	100.00%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7454 and 0.6494
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	9353 / 0 / 527
Goodness-of-fit on F ²	1.064
Final R indices [I > 2σ(I)]	R1 = 0.0543, wR2 = 0.1514
R indices (all data)	R1 = 0.0670, wR2 = 0.1637
Largest diff. peak and hole	2.211 and -2.214 e.Å ⁻³

Table S3. XYZ coordinate of the optimized structure of **3**.

Sb	0.017843	1.744687	0.260828	H	0.225767	-3.144004	-1.992253
Sb	1.814795	-1.429886	0.115287	C	3.976176	-0.397452	-4.256165
Cl	-2.275884	-1.360945	-3.031407	H	4.494893	-0.143501	-5.173731
Cl	-3.655347	-0.346972	3.050583	C	3.953860	-1.117816	2.271366
Cl	-4.952947	-2.606384	-1.798715	H	3.643432	-0.079856	2.218969
Cl	-5.636692	-2.108844	1.262281	C	5.343470	-2.861987	3.230412
O	-1.243188	0.602837	1.527926	H	6.125904	-3.165999	3.918341
O	-0.620472	0.113990	-0.987555	C	1.230428	3.728927	-1.891051
C	2.641463	-1.141570	-1.802820	H	0.618430	4.461507	-1.374410
O	1.508668	0.318943	0.782173	C	3.701106	-3.430558	1.538955
C	-1.805875	-0.402246	-0.538589	H	3.205645	-4.181964	0.930918
C	-3.303803	-0.669594	1.362842	C	4.713302	-3.818451	2.424499
C	3.251301	0.510003	-3.521715	H	5.003995	-4.862075	2.488146
C	1.278480	2.387005	-1.394763	C	4.962519	-1.516392	3.156128
C	-0.125543	-3.416629	1.407416	H	5.445762	-0.778089	3.787627
H	0.223696	-2.977642	2.336366	C	0.347415	-2.954710	0.166471
C	3.325186	-2.078194	1.459618	C	-2.214523	2.842867	-1.635250
C	3.396568	-2.095522	-2.557825	H	-1.786873	2.134147	-2.337254
H	3.489925	-3.117968	-2.205606	C	-2.255757	3.875662	0.559399
C	1.922257	4.130670	-3.035969	H	-1.862784	3.975273	1.566188
H	1.845823	5.164218	-3.359109	C	-1.679792	2.960963	-0.339286
C	2.578214	0.132840	-2.315415	C	0.155159	2.708785	3.215480
C	4.028422	-1.729591	-3.743101	H	-0.665846	2.013815	3.347120
H	4.589413	-2.479698	-4.291221	C	1.829974	3.741473	1.790187
C	-3.868723	-1.662908	-0.789265	H	2.309890	3.856873	0.823209
C	-2.684509	-1.130905	-1.338623	C	0.750807	2.855003	1.948923
C	-4.172727	-1.438052	0.562444	C	-3.345520	4.663790	0.166606
C	2.703573	3.224679	-3.807655	H	-3.784033	5.366259	0.869085
H	3.209028	3.555064	-4.708279	C	-3.871034	4.541482	-1.124856
C	2.067504	1.540335	-2.141380	H	-4.718549	5.149249	-1.427017
C	-1.054575	-4.555742	-0.986619	C	-3.305461	3.629704	-2.024573
H	-1.424922	-4.985671	-1.910754	H	-3.714874	3.526154	-3.024943
C	-1.070965	-4.447091	1.440286	C	0.632879	3.451345	4.302931
H	-1.451943	-4.796398	2.393866	H	0.168103	3.334591	5.277359
C	2.750951	1.933837	-3.337014	C	2.303295	4.480853	2.881868
C	-2.124422	-0.151170	0.822699	H	3.137309	5.163707	2.749531
C	-1.532329	-5.015875	0.246120	C	1.703971	4.338123	4.138556
H	-2.271984	-5.808850	0.276438	H	2.070138	4.912472	4.984174
C	-0.115243	-3.519086	-1.033201				

Reference

1. S. M. Kilyanek, X. Fang and R. F. Jordan, *Organometallics*, 2009, **28**, 300-305.