

A Five-Membered PdSb_n Coordination Series

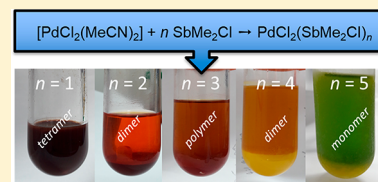
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Supporting Information

ABSTRACT: Five complexes of the general formula PdCl₂(SbMe₂Cl)_n (*n* = 1–5) have been synthesized by combining [PdCl₂(MeCN)₂] and SbMe₂Cl in different molar ratios in toluene. Their solid-state structures have been determined by X-ray crystallography. The complexes display considerable structural diversity: [Pd₄Cl₈(SbMe₂Cl)₄] (**1**, *n* = 1) is a chloride-bridged tetramer; [Pd₂Cl₄(SbMe₂Cl)₄] (**2**, *n* = 2) is a dimer; [PdCl(SbMe₂Cl)₂(SbMe₂Cl₂)] (**3**, *n* = 3) is a supramolecular polymer; [Pd₂(SbMe₂Cl)₈]Cl₄ (**4**, *n* = 4) is a loosely associated dimer, and [Pd(SbMe₂Cl)₅]Cl₂ (**5**, *n* = 5) is a monomer with square-pyramidal PdSb₅ coordination geometry. Each structure contains secondary interactions between coordinated Sb centers and chloride ligands or anions, resulting in five-coordinate Sb in all cases with a range of Sb⋯Cl bond lengths. The electronic structures of these complexes have been investigated using DFT methods including NBO and Pipek–Mezey localized orbital methods in order to interrogate both the Sb–Pd and secondary Sb⋯Cl bonding.



INTRODUCTION

Molecules containing a Lewis acidic main group metal (E) in close proximity to a transition metal (M) have received significant recent attention, particularly examples in which M–E interactions can be used to mediate the electronic properties of M. This can lead to stabilization of unusual structures and manifestation of new or enhanced cooperative catalytic properties.^{1–5} In the majority of cases, these are best characterized as M→E interactions, in which M donates electron density to a strongly Lewis acidic E center. We have an interest in Lewis amphoteric main group ligands, which behave as electron donors toward M (E→M), while also retaining some Lewis acidic character at E. This behavior is most often observed in complexes of organoantimony ligands, in which Sb(III) centers coordinate to a transition metal via a lone pair while also forming secondary coordinative bonds with available nearby donor atoms (N, O, halides) (Figure 1a).^{6–9}

Sb–M (M = late transition metal) complexes can demonstrate unforeseen reactivity arising from the non-innocence of antimony ligands with respect to redox or coordination, as demonstrated by Gabbai's extensive work on tethered Sb–M systems, leading to potential applications in catalysis, solar energy storage, and anion sensing.^{3,10–16} In particular, the strong affinity of Sb for halide anions (X[−]) means that the formation of Sb–X bonds is often favored over the formation of M–X bonds.

The introduction of covalently bonded halide substituents at Sb increases the Lewis acidity of the antimony center, making halostibines SbR₂X attractive ligands for investigation of Lewis amphoteric behavior. We have previously reported one of the first examples of a halostibine complex with a transition metal halide, [Pd₂Cl₄(SbMe₂Cl)₄] (**2**, Figure 1b), a dimer in the solid state with two eclipsing square planes held together by

secondary Cl→Sb interactions.¹⁷ Reaction of this complex with MeLi results in the formation of the Pd(0) tetramer [Pd₄(SbMe₃)₈], an unprecedented example of μ₃-bridging by a pnictine ligand (Figure 1b).

Here, we report an unusual coordination series of five complexes with the general formula PdCl₂(SbMe₂Cl)_n (*n* = 1–5), of which **2** is one member (*n* = 2), formed by reacting the same ligand and metal precursor in five different molar ratios. All show Lewis amphotericism of the Sb centers, with either intra- or intermolecular secondary interactions which direct their solid-state structures, leading in four cases to supramolecular architectures. These complexes encompass five different coordination environments of Pd: four square-planar with PdSb_nCl_(4–n) coordination and, most remarkably, the square-pyramidal Pd(II) complex **5** which displays homoleptic PdSb₅ coordination. This series represents a significant increase in known transition metal complexes with halostibines and provides an opportunity to investigate and characterize both Sb–M bonding and secondary Cl→Sb bonding in this type of complex.

RESULTS AND DISCUSSION

By combining SbMe₂Cl (L) with [PdCl₂(MeCN)₂] (M) in toluene in a range of L/M ratios, five different complexes (**1**–**5**, Scheme 1) were isolated with Sb/Pd ratios of 1:1, 2:1, 3:1, 4:1, and 5:1, and their solid-state structures were determined by X-ray crystallography. The structure of each complex is stabilized by secondary Cl→Sb interactions formed by coordinated Sb centers accepting electron density from chloride ligands or anions. The bonding situation in these

Received: August 2, 2018

Published: October 8, 2018

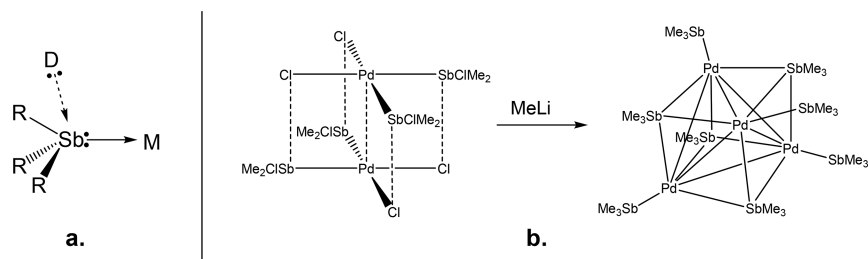
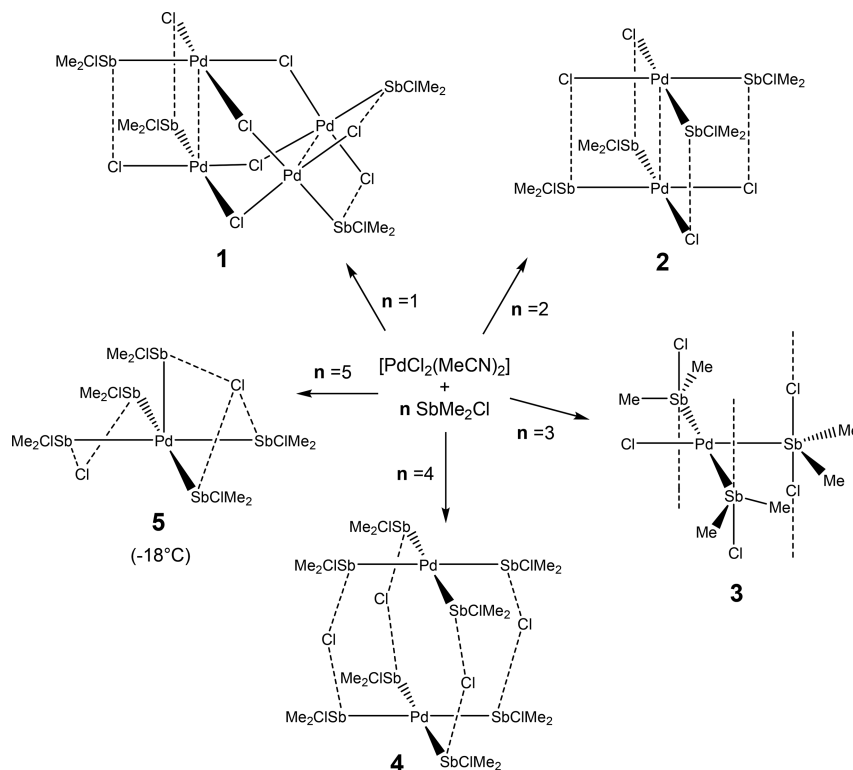


Figure 1. (a) Lewis amphoteric behavior of a stibine ligand ($D =$ donor atom, $M =$ transition metal). (b) Reaction of the dimeric $[\text{Pd}_2\text{Cl}_4(\text{SbMe}_2\text{Cl})_4]$ (**2**, secondary bonding indicated by dashed lines) to form the $[\text{Pd}_4(\text{SbMe}_3)_8]$ cluster.¹⁷

Scheme 1. Synthesis of Complexes 1–5 Including Diagrammatic Representation of Their Solid-State Structures



complexes has been elucidated by DFT analysis of their electronic structure.

Combining 1 equiv of ligand with the metal precursor resulted in the formation of a near-insoluble red-brown solid, identified by X-ray diffraction as $[\text{Pd}_4\text{Cl}_8(\text{SbMe}_2\text{Cl})_4]$ (**1**), a tetrameric complex with a 1:1 Sb/Pd ratio. The solid-state structure of **1** (Figure 2) contains two pairs of Pd atoms, each pair held together by a combination of one metallophilic $\text{Pd}\cdots\text{Pd}$ contact (mean $\text{Pd}-\text{Pd}$ 3.062 Å) and two secondary $\text{Cl}\rightarrow\text{Sb}$ interactions between the Cl and SbMe_2Cl ligands on each Pd (mean $\text{Sb}-\text{Cl}$ 2.947 Å). The two pairs are linked by a total of four $\text{Pd}-\text{Cl}-\text{Pd}$ bridges (mean $\text{Pd}-\text{Cl}$ 2.365 Å), forming a distorted gyrobfastigium¹⁸ Pd_4Cl_4 core. Despite the pseudo- S_4 symmetry of the molecule (Figure 2, inset), each of the four $\text{PdCl}_2(\text{SbMe}_2\text{Cl})$ units is crystallographically independent. Comparison of the bond lengths and angles shows them to be essentially chemically identical, with the largest variation being a spread of 0.17 Å in the $\text{Sb}\cdots\text{ClPd}$ distances (Table S7).

As previously reported,¹⁷ combination of the same two reagents in a 2:1 Sb/Pd ratio gives the red dimer $[\text{Pd}_2\text{Cl}_4(\text{SbMe}_2\text{Cl})_4]$ (**2**). Recrystallization of this complex from benzene or dichloromethane results in the formation of

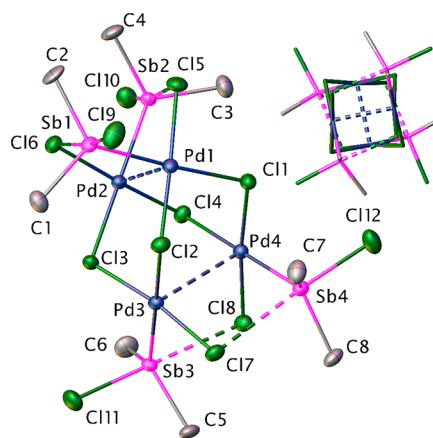


Figure 2. View of the structure of $[\text{Pd}_4\text{Cl}_8(\text{SbMe}_2\text{Cl})_4]$ (**1**); ellipsoids are drawn at 50% probability levels, and H atoms are omitted for clarity. Secondary interactions are indicated by dashed bonds. Inset: Wireframe representation of the view down the pseudo- S_4 axis.

the respective solvates, $2\cdot\text{C}_6\text{H}_6$ and $2\cdot 2\text{CH}_2\text{Cl}_2$ (Figure 3), whose solid-state structures both contain centrosymmetric

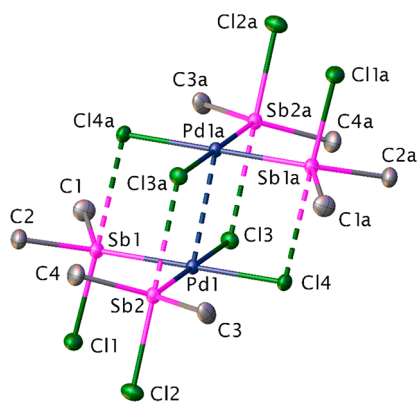


Figure 3. View of the $[\text{Pd}_2\text{Cl}_4(\text{SbMe}_2\text{Cl})_4]$ component of the structure of $2 \cdot 2\text{CH}_2\text{Cl}_2$; ellipsoids are drawn at 50% probability levels, and H atoms are omitted for clarity. Secondary interactions are indicated by dashed bonds. Symmetry operation: $a = 1 - x, 1 - y, -z$.

dimeric units similar to that found in the unsolvated complex. Though most bond lengths in the three structures are comparable (Tables S8–S11), there is a notable difference in the bond angles around the Sb centers, with Cl–Sb–Cl torsion angles ranging from $27.74(3)^\circ$ in the unsolvated structure to $2.65(3)^\circ$ in the CH_2Cl_2 solvate, with the benzene solvate having an intermediate value of $9.21(6)^\circ$ (Figure 4).

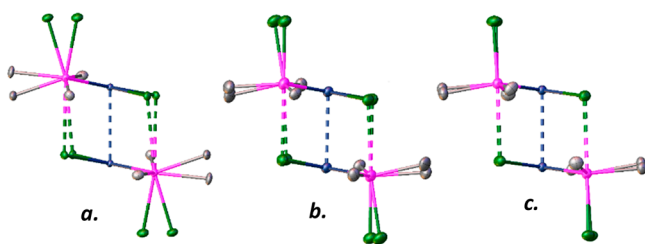


Figure 4. View down the Sb–Sb vector of **2**, with the Pd...Pd axis lying vertical in the plane of the page in (a) **2**; (b) $2 \cdot 4\text{C}_6\text{H}_6$; (c) $2 \cdot 2\text{CH}_2\text{Cl}_2$.

There is no evidence of any significant interaction between the dimers and the solvent molecules, so these small differences in structure are most likely to be due to packing effects. The dimers are supported by both Pd...Pd and Cl→Sb interactions, with the resulting four-membered (–Pd–Sb...Cl–Pd–) ring motif being comparable with that found in complex **1**, with a slightly shorter average Pd...Pd distance (2.918 \AA across all three structures, compared to 3.062 \AA). In one case, a few yellow crystals were isolated from the second filtrate of this reaction, which were analyzed by X-ray crystallography and proved to be the 4:1 L/M complex $[\text{Pd}_2(\text{SbMe}_2\text{Cl})_8]\text{Cl}_4$ (**4**, vide infra).

Increasing the ratio of SbMe_2Cl and $[\text{PdCl}_2(\text{MeCN})_2]$ to 3:1 in the reaction mixture results in the isolation of an orange-yellow crystalline solid **3**. The asymmetric unit of the solid-state structure has the formula $[\text{PdCl}(\text{SbMe}_2\text{Cl})_2(\text{SbMe}_2\text{Cl}_2)]$, with a 1:3 ratio of Pd/Sb (Figure 5a). The distorted square-planar Pd center is coordinated by one chloride and two SbMe_2Cl ligands, as well as a moiety which can be tentatively considered as the $\text{SbMe}_2\text{Cl}_2^-$ ligand, the result of insertion of a third equivalent of SbMe_2Cl into a Pd–Cl bond. The geometry around Sb in this ligand is close to trigonal-bipyramidal, with the two Cl substituents *trans* (Cl–Sb–Cl = $176.70(5)^\circ$) and

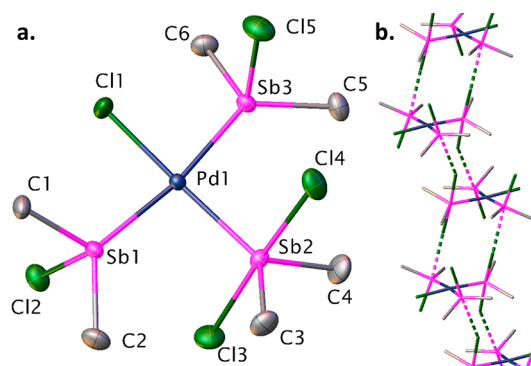


Figure 5. (a) View of the asymmetric unit of **3**; ellipsoids are drawn at 50% probability levels, and H atoms are omitted for clarity. (b) Wireframe representation of a section of the 1D ladder structure of **3**. Secondary interactions are indicated by dashed bonds.

the two Sb–Cl distances nearly equal ($2.538(1) \text{ \AA}$ and $2.590(1) \text{ \AA}$) and longer than those in the SbMe_2Cl coligands by around 0.2 \AA . The two Me substituents lie in an equatorial plane with the Pd center, with the C–Sb–C angle ($106.3(2)^\circ$) notably smaller than the C–Sb–Pd angles (mean 126.8°). The only previous complex of this ligand to be structurally characterized is $[\text{FeCp}(\text{CO})(\text{PMe}_3)(\text{SbMe}_2\text{Cl}_2)]$,¹⁹ obtained by oxidation of the SbMe_2^- ligand in situ, which has a similar geometry around Sb and a slightly longer mean Sb–Cl distance of 2.601 \AA .

Individual molecules of **3** are linked together by Cl→Sb interactions between the Sb atoms of the SbMe_2Cl ligands and the Cl atoms of the $\text{Sb}_2\text{MeCl}_2^-$ ligands, resulting in a 1D polymeric chain structure (Sb3–Cl3 = 3.167 \AA , Sb1–Cl4 = 3.046 \AA). Each molecule forms a total of four intermolecular interactions, two above and two below the square plane, to give a ladder configuration (Figure 5b). In contrast to the structures above, no palladophilic interactions are observed, with the Pd centers in neighboring molecules being offset from each other with respect to the axis of chain formation (Pd–Pd distances = $6.188, 6.409 \text{ \AA}$).

It is notable that despite the solid-state structure containing two different Me environments, this complex dissolves in dichloromethane to give an orange solution with only one peak observed in both the ^1H and ^{13}C NMR spectra, suggesting that this structure is not retained in solution, or that ligand exchange is fast for both the SbMe_2Cl and $\text{SbMe}_2\text{Cl}_2^-$ ligands. It is also possible that the two ligand types are interchangeable in solution, with Cl being exchanged between Sb centers on the NMR time scale. Complex **3** seems stable as a solid in air over a period of days, retaining its appearance and structure (according to X-ray powder diffraction).

A detailed analysis of the electronic structure of compound **3** has been undertaken in order to elucidate the nature of the Pd–L bonding. The geometries of **3** and other complexes discussed in this section were optimized (RI-BP86-D3/def2-TZVP(ecp)) prior to analysis of their electronic structures by means of the natural bond orbital (NBO) and Pipek–Mezey (PM) localized orbital methods. All calculations were performed in vacuo on the isolated molecules. Optimized key bond metrics (Pd–Sb = $2.54\text{--}2.56 \text{ \AA}$; Pd–Cl1 = 2.35 \AA) are in excellent agreement with their crystallographic counterparts (Table S5), also well reproducing the trigonal-bipyramidal geometry around Sb2 (Sb2–Cl3/Cl4 = 2.54 \AA ; Cl3–Sb2–Cl4 = 177.2° , C3–Sb2–C4 = 108.6°). Although

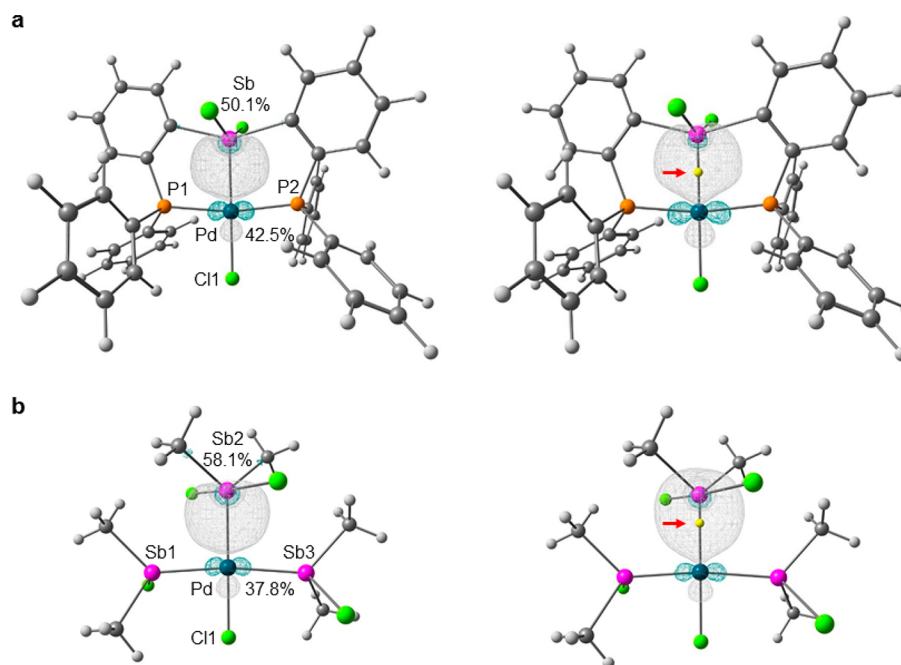


Figure 6. Isosurface plots (cutoff 0.05 au) of NLMOs (left) and Pipek–Mezey localized orbitals (right) for the Pd–Sb interaction in (a) $[(o\text{-dppp})_2\text{Cl}_2\text{SbPdCl}]$ and (b) complex **3**. Charge centroids of Pipek–Mezey localized orbitals are shown as yellow dots (red arrows are provided as a guide for the eye). Each dot accounts for two electrons.

the Sb(III) oxidation state and dative character of the SbMe_2Cl ligands seems unambiguous, the situation is less clear-cut for the SbMe_2Cl_2 moiety, where the bonding interaction may lie on a continuum between covalent and dative depending on the Sb oxidation state. The recently reported $[(o\text{-dppp})_2\text{Cl}_2\text{SbPdCl}]^{20}$ ($o\text{-dppp} = o\text{-(Ph}_2\text{P)C}_6\text{H}_4$) contains an analogous $\text{R}_2\text{Cl}_2\text{SbPd}$ motif within a polydentate ligand framework, and the Pd–Sb interaction has been characterized as a nonpolar covalent bond between formal Sb(IV) and Pd(I) centers, based on analysis of the natural localized bond orbitals (NLMO) of the Pt homologue.¹¹

In the present study, an alternative molecular orbital localization scheme based on the PM criterion was utilized in addition to the NBO analysis. The former procedure provides not only the shape of the orbital but also its centroid of charge, which can be used to establish the electron counts of the bonding atoms. For covalent two-center bonds, the orbital charge centroid sits approximately at the center of the bond vector, whereas in dative interactions, the charge center is moved closer toward the donor atom.^{21,22}

The $[(o\text{-dppp})_2\text{Cl}_2\text{SbPdCl}]$ complex serves as a convenient reference point and is therefore revisited here. The NLMO of the Pd–Sb interaction in $[(o\text{-dppp})_2\text{Cl}_2\text{SbPdCl}]$ (Figure 6a) is consistent with a covalent σ -type Sb–Pd bond, with orbital contributions of both atoms (Pd 42.5%; Sb 50.1%) being similar to those of the Pt homologue (Pt 45.0%; Sb 49.0%). In both cases, the σ -bond is slightly polarized toward antimony.³ This view finds further support in the corresponding PM localized orbital, with a near tubular shape along the bond vector and a charge centroid positioned nearly equidistantly between the Pd and Sb atoms (Figure 6a).

In contrast, the PM orbitals and charge centers associated with the Pd–P and Pd–Cl bonds in this complex are notably more displaced toward the P and Cl donors (Figure S2). The dative character of these bonds is also reflected in the associated low Mulliken electron populations on the Pd atom

(Table S1), whereas the electron populations associated with the Pd–Sb bond again display only a slight polarization toward the Sb center. The situation differs for complex **3**, in which all PM localized orbitals have more pronounced “pear shapes” weighted toward the donor atoms (Figure S4). The Pd1–Sb2 interaction is very similar to the lone pair dative bonds linking the other donor atoms to Pd, and the charge centroid is notably shifted toward Sb2 (Figure 6b). The corresponding NLMO converges to the same result, with orbital contributions of both atoms (Pd1 37.8%; Sb3 58.1%) pointing to a dative bond. The resemblance to the bonds involving the SbMe_2Cl ligands is also borne out in the Mulliken populations, which are virtually identical for all three Pd–Sb bonds (Table S2, Pd ~ 0.45 , Sb ~ 1.65). Thus, the above analysis is in this case fully consistent with a Pd(II) center ligated by a $\text{Sb}^{\text{III}}\text{Me}_2\text{Cl}_2^-$ ligand, and the complex is best described as $[\text{Pd}^{\text{II}}\text{Cl}(\text{Sb}^{\text{III}}\text{Me}_2\text{Cl}_2^-)(\text{Sb}^{\text{III}}\text{Me}_2\text{Cl}_2)]$. It is interesting to notice that the phenylene bridge in $[(o\text{-dppp})_2\text{Cl}_2\text{SbPdCl}]$ gives rise to a wider C–Sb–C angle (151.2°), whereas the Cl–Sb–Cl angle becomes more obtuse (151.8°) compared to the corresponding angles in **3** (108.6° and 177.2°). As a result, the approximately trigonal-bipyramidal Sb center in **3** ($\tau_5 \sim 0.86$) is distorted toward a square-pyramidal geometry ($\tau_5 \sim 0.0$) in $[(o\text{-dppp})_2\text{Cl}_2\text{SbPdCl}]$. This “ C_{4v} distortion” along the described coordinate reduces the proportion of s-character in the σ Pd–Sb bond (28.1%, cf. 39.2% in **3**), which in turn renders the bond less polarized. The presence of a hypervalent $\text{SbMe}_2\text{Cl}_2^-$ “ate” fragment again appears the best description in $[\text{Fe}^{\text{II}}\text{Cp}(\text{CO})(\text{PMe}_3)(\text{SbMe}_2\text{Cl}_2)]$, which was also modeled for qualitative comparison (Figures S12 and S13).

Combination of the precursors in a 4:1 L/M ratio rapidly generates a fine, intensely lemon-yellow precipitate. Isolation of this solid followed by drying in vacuum for 1 h results in a slight darkening of the color to orange-yellow. Powder X-ray diffraction of this solid identifies one crystalline phase closely matching the structure of **3** (Figure S15). However, a few small

yellow crystals of a dimeric complex with a 4:1 Sb/Pd ratio, $[\text{Pd}_2(\text{SbMe}_2\text{Cl})_8]\text{Cl}_4 \cdot 2\text{C}_7\text{H}_8$ (**4**, Figure 7), were isolated as a

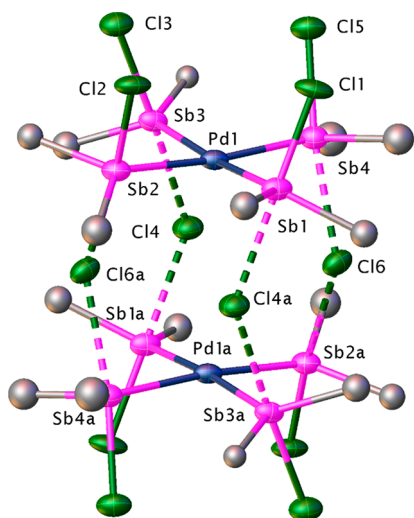


Figure 7. View of **4** from the structure of $4 \cdot 2\text{C}_7\text{H}_8$. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. C atoms were refined isotropically. Symmetry operation: $a = 1 - x, 1 - y, 1 - z$. Secondary interactions are indicated by dashed bonds.

minor product from the (presumably ligand rich) filtrate from the synthesis of **2**. Due to the correspondence in stoichiometry and color, it is presumed that this complex is also a product of the 4:1 reaction, which decomposes under vacuum to generate **3**. Attempts to crystallize **4** in bulk using a variety of solvents and temperatures led only to the isolation of a fine yellow powder, sometimes accompanied by a few crystals of the orange **3** (vide supra) or green **5** (vide infra) complexes. The single-crystal X-ray data obtained for **4** are of poor quality, and although it allows identification of the structure and connectivity of the complex without doubt, an in-depth analysis of the structural parameters from these data is not appropriate.

The structure is composed of two symmetry-related homoleptic square planar $[\text{Pd}(\text{SbMe}_2\text{Cl})_4]^{2+}$ cations, with four chloride anions “sandwiched” between them, each chloride forming two $\text{Cl} \rightarrow \text{Sb}$ interactions, one with each cation. The Me substituents of the ligands are found close to the square plane, whereas the four Cl substituents all face out of the plane on the same side, approximately *trans* to the four longer $\text{Cl} \rightarrow \text{Sb}$ interactions on the opposite side. The only other structurally characterized example of a Pd(II) complex with an Sb_4 coordination sphere is in $[\text{Pd}\{1,2\text{-C}_6\text{H}_4(\text{CH}_2\text{SbMe}_2)_2\}_2][\text{PF}_6]_2$,²³ in which two bidentate distibines chelate the Pd center. Though the poor quality of our data precludes detailed comparison of the structural parameters, the Sb–Pd bond distances are very similar, averaging around 2.57 Å in both structures. The geometry of **4** has been optimized by DFT methods, and the parameters obtained agree well with the X-ray structure (Table S5). The biggest discrepancy is in the long Pd–Pd distance, which is calculated to be 0.26 Å shorter than observed in the X-ray data. The Sb...Cl distances are in good agreement, indicating that this is not a result of overestimation of $\text{Cl} \rightarrow \text{Sb}$ interaction strength but rather correlates with a slight underestimate of the Sb–Cl–Sb angles.

Combining greater than 4 equiv of SbMe_2Cl with 1 equiv of $[\text{PdCl}_2(\text{MeCN})_2]$ in toluene at room temperature likewise precipitates a yellow product, which, similarly to the 4:1 reaction, gives crystals of **3** after drying under vacuum, though the elemental analysis of the bulk product suggests higher ligand content. However, refrigeration of the initial filtrate at -18°C causes the solution to become a deep green color, which on warming back to room temperature reverts to the original yellow. This reversible color change could be observed repeatedly by cooling and warming the solution. Storage of the solution at -18°C for several days allowed the isolation of a few green-black crystals, which appeared to be stable at room temperature under fomblin oil for several days.

The structure was determined by X-ray diffraction and shows the highly unusual monomeric complex $[\text{Pd}(\text{SbMe}_2\text{Cl})_5]\text{Cl}_2$ (**5**, Figure 8), in which 5 equiv of the

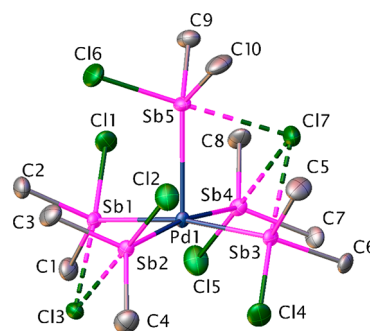


Figure 8. View of the structure of **5**; ellipsoids are drawn at 50% probability levels, and H atoms are omitted for clarity. Secondary interactions are indicated by dashed bonds.

SbMe_2Cl ligand are coordinated to one Pd center in a distorted square-pyramidal geometry. The Pd atom sits only 0.23 Å above the square plane defined by the four equatorial ligands. The Sb–Pd bond length for the axial ligand ($\text{Sb5-Pd1} = 2.971(1)$ Å) is significantly greater than that for the equatorial ligands (2.593–2.599 Å) and somewhat greater than the sum of the covalent radii ($\sum r_{\text{cov}} = 2.78$ Å),²⁴ though much shorter than the sum of the van der Waals radii ($\sum r_{\text{vdW}} = 4.62$ Å).²⁵ This weaker coordinate bond undoubtedly reflects the energy penalty of disrupting the favored square-planar ligand field for the d^8 metal center by introducing axial coordination. The two chloride anions form close contacts with the Sb centers of the ligands, this time in an intramolecular fashion, with one chloride bridging two *cis* equatorial ligands below the square plane and the other bridging the remaining three ligands (two equatorial and one axial) above the plane. Each ligand is arranged so that the covalent Sb–Cl substituent is roughly *trans* to the coordinated chloride anion. This gives the molecule a pseudo-mirror plane perpendicular to the equatorial square plane ($[\text{Sb1}, \text{Sb2}, \text{Sb3}, \text{Sb4}] \perp [\text{Pd1}, \text{Sb5}, \text{Cl6}, \text{Cl7}, \text{Cl3}] = 90.0^\circ$), which bisects the two chloride anions, the axially coordinated ligand, and the angles between two *cis* pairs of equatorial ligands, though attempts to model the structure in a higher symmetry space group were unsuccessful. Literature precedent for square-pyramidal Pd(II) complexes is mostly confined to examples in which the architecture of a polydentate ligand sterically constrains the coordination geometry^{26–28} or where a halide occupies the apical position with a long bond distance.^{29,30} To our knowledge, there are no other examples of homoleptic

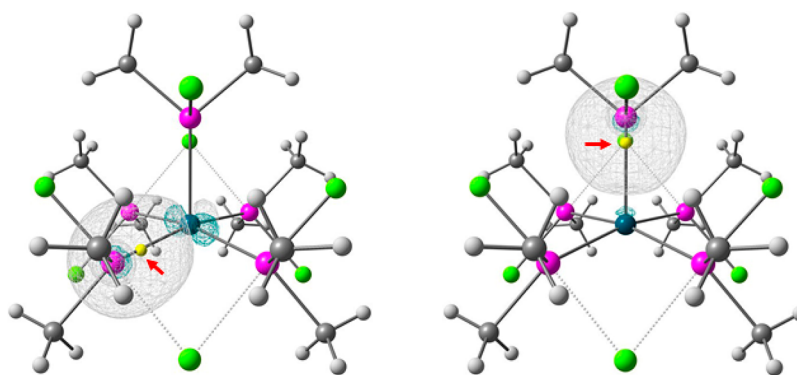


Figure 9. Isosurface plots (cutoff 0.05 au) of Pipek–Mezey localized orbitals for the basal (left) and apical (right) Pd–Sb interactions in complex 5. Charge centroids are shown as yellow dots (red arrows are provided as a guide for the eye). Each dot accounts for two electrons.

square-pyramidal Pd(II) complexes with monodentate ligands. Presumably upon warming to room temperature in solution, the weakly associated axial fifth ligand becomes dissociated, returning the complex to a four-coordinate, square-planar configuration and triggering the reversible change in color.

The nature of the Pd–Sb interactions in complex 5 has been probed using the same methods outlined above for complex 3. The distorted square-pyramidal geometry is well reproduced in the DFT-optimized structure, with the Pd atom displaced by 0.27 Å above the center of the equatorial ligand plane. Optimized bond distances are in good agreement with experiment. The asymmetry between the basal Pd–Sb (2.61–2.62 Å) and apical Pd–Sb bond lengths (2.80 Å) is reproduced by the calculations, although the latter is somewhat underestimated compared to the single-crystal X-ray data (2.971(2) Å). The bond distances between the chloride anions and the Sb centers of the ligands (Sb⋯Cl = 2.77–3.17 Å) are also in reasonably good agreement with the experimental values (2.772(4)–3.027(4) Å).

Both NBO analysis and PM localization predict the presence of lone-pair dative bonds linking the basal Sb centers to the Pd atom (Figure 9 and Figure S5), comparable to those observed in 3. On the other hand, the apical Pd–Sb bond may be best described as $1p_{Sb5} \rightarrow Pd \sigma^*_{Pd-Sb}$ donor–acceptor interactions ($\sum \Delta E^{(2)} = 57.1 \text{ kcal mol}^{-1}$), involving antibonding Pd sd hybrid orbitals. The lone pair located on the Sb center obtained from the PM localization procedure is shown in Figure 9. Importantly, there is no indication of any Pd→ p_{Sb} interaction that would support the presence of a Lewis acidic Z-type stiborane ligand. The above analysis is consistent with the experimental result and clearly distinguishes between two different bond types in the complex, with a weaker bound apical ligand.

Secondary intramolecular donor–acceptor interactions between the Cl[−] anions and the coordinated SbMe₂Cl ligands were also readily identified by NBO analysis (see Figure S7 for isosurface plots of key donor–acceptor orbital pairs). The bridging chloride Cl3 is largely stabilized through donation of electron density from one of its 3p donor orbitals into the *trans* σ^*_{Sb-C} orbitals on the two adjacent SbMe₂Cl units ($\Delta E^{(2)} = 20.7$ and $22.3 \text{ kcal mol}^{-1}$ for Sb1 and Sb2, respectively). Likewise, two such $3p_{Cl} \rightarrow \sigma^*_{Sb-Cl}$ interactions are observed for Cl7 interacting with the two equatorial stibine fragments. The larger distance between Cl7 and these Sb acceptors (~2.92 Å) compared to that of Cl3 (~2.77 Å) is reflected in a smaller interaction energy ($\Delta E^{(2)} = 13.4$ and $12.9 \text{ kcal mol}^{-1}$ for Sb3 and Sb4, respectively). However, a third interaction between

an orthogonal $3p_{Cl}$ donor orbital and the σ^*_{Sb-Cl} acceptor orbital located on the axial SbMe₂Cl unit ($\Delta E^{(2)} = 11.0 \text{ kcal mol}^{-1}$) adds to the overall stabilization energy ($\sum \Delta E^{(2)} = 37.3 \text{ kcal mol}^{-1}$), rendering it similar in magnitude to the sum of the interactions between Cl3 and Sb1/Sb2 ($\sum \Delta E^{(2)} = 43.0 \text{ kcal mol}^{-1}$). Secondary interactions similar to those found in 5 are also the main contributing factor in supporting the structures of 1 and 2 (Figures S8 and S10). The approximate *trans* orientation of Pd-bound Cl[−] and the Sb–Cl bond of the SbMe₂Cl group on adjacent complex fragments maximizes the $3p_{Cl} \rightarrow \sigma^*_{Sb-Cl}$ orbital interactions ($\Delta E^{(2)} \sim 20 \text{ kcal mol}^{-1}$ /pair), which we have previously demonstrated for the 2:1 L/M complex 2 in this series.¹⁷ Additional stabilization in both the tetrameric and dimeric complexes is provided by *cis* $3p_{Cl} \rightarrow \sigma^*_{Sb-C}$ ($\Delta E^{(2)} = 2\text{--}4 \text{ kcal mol}^{-1}$ /pair) and $4d_{Pd} \rightarrow \sigma^*_{Pd-L}$ ($\Delta E^{(2)} = 0.1\text{--}2.5 \text{ kcal mol}^{-1}$ /pair) interactions. The latter involve mutual donation of electron density from Pd lone pairs (d-orbitals) into antibonding Pd–ligand σ^* orbitals centered on neighboring Pd centers. Detailed analysis of canonical and localized molecular orbitals for 1 and 2, however, does not support the presence of any significant direct Pd–Pd bonding interaction in these complexes (Figures S9 and S11 and Table S4).

Secondary Bonding at Sb. In all five complexes, each SbMe₂Cl ligand forms one secondary Cl→Sb interaction, in every case disposed approximately *trans* to the covalent Sb–Cl bond (mean Cl–Sb⋯Cl = 174.4°). This is consistent with the acceptor behavior of the SbMe₂Cl ligand observed in other complexes toward heteroatoms (O, F) from “weakly coordinating” anions, which also coordinate *trans* to the Sb–Cl bond.⁶ The complex [CpFe(CO)(Me₂BrSb- μ -Br-SbBrMe₂)] also displays very similar interactions between a bromide anion and the related bromostibine ligand, particularly reminiscent of the (−Pd1–Sb1–Cl3–Sb2−) ring found in 5.⁷ As discussed above, this behavior is attributable to the availability of the low-lying σ^* Sb–X orbital on the halostibine ligand, which acts as an acceptor orbital. The structurally characterized series of complexes described here presents a unique opportunity to compare several examples of secondary interactions between the same ligand with the same metal halide, all in similar coordination environments. Interatomic distances for the secondary Cl→Sb interactions in these complexes range between 2.75 and 3.17 Å ($\sum r_{vdW} = 4.29 \text{ Å}$, $\sum r_{cov} = 2.78 \text{ Å}$).^{25,24} Plotting these distances for all seven structures against the *trans* covalent Sb–Cl distance for each Sb atom reveals a clear linear trend with a negative gradient (Figure 10), consistent with the increased population of the

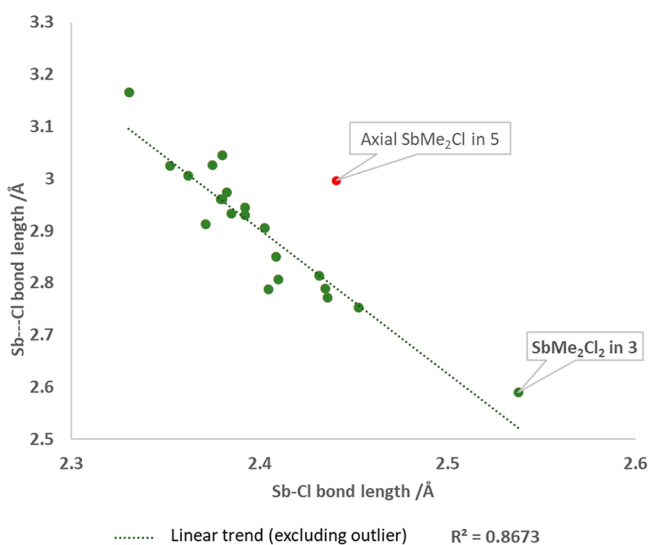


Figure 10. Graph showing secondary Sb...Cl bond distances vs the *trans* covalent Sb-Cl distances for all Sb atoms in compounds 1–5.

$\sigma_{\text{Sb-Cl}}^*$ orbital as a result of a stronger Cl→Sb interaction, weakening the *trans* covalent Sb-Cl bond. This corroborates a significant involvement of orbital interactions in forming these secondary, “hypervalent” bonds rather than their being entirely the result of electrostatic interactions.

There is one main outlier which was excluded from the fit, namely the Sb center that is coordinated in the axial position in the structure of **5**. This discrepancy can be explained by the significantly different coordination environment of this Sb center with respect to Pd when compared to the other SbMe₂Cl ligands. Notably, plotting the two nearly equal Sb-Cl distances around the SbMe₂Cl₂ ligand in **3** gives a point which lies in good agreement with the general linear trend, suggesting that this ligand can alternatively be viewed as the result of a strong interaction between a Cl[−] anion and a SbMe₂Cl ligand, analogous to the weaker interactions of the same nature seen in **4** and **5** but to the extent that a near symmetrical three-center/four-electron bond is formed.

Solution Behavior. In toluene solution, each complex retains the characteristic color of the corresponding solid, though there is a slight change of color when complexes 1–3 are dissolved in dichloromethane. The ¹H and ¹³C NMR spectra of 1–3 are almost indistinguishable, each containing a single peak at around 2.1–2.2 ppm (¹H NMR) and 16–18 ppm (¹³C NMR), consistent with a single ligand environment. It is probable that the complexes are fluxional in solution, with the labile SbMe₂Cl ligands exchanging fast on the NMR time scale and the prevalent structure (and hence color) depending on the L/M ratio in solution. UV–vis electronic spectra (Figures S16 and S17 and Table S17) in dichloromethane solution differ significantly between the three compounds, each displaying two main bands, with those of **1** lying the lowest in energy followed by **2** then **3**. The solid-state spectra are somewhat different, each containing several broad overlapping bands in the 300–600 nm region. To investigate the interconversion of the five compounds in solution, 5 equiv of the ligand in a toluene stock solution was sequentially added to the metal precursor, interspersed by 30–40 min periods of stirring between each equivalent. The color of the solution changed through red-brown after 1 equiv to red after the second, orange after the third, and yellow after the fourth,

suggesting these complexes interconvert with facility in solution. Adding a fifth equivalent results in a slight color change to a less warm yellow, which on refrigeration at −18 °C becomes the characteristic intense green of complex **5** (Figure S18).

CONCLUSIONS

Complexes 1–5 represent a rare example of a coordination series in which the same metal fragment (PdCl₂) complexes the same ligand (SbMe₂Cl) in five different stoichiometries, without the presence of other coligands. Whereas complexes 1–3 are fairly robust, even air stable in the case of **3**, complexes **4** and **5** are unstable with respect to loss of ligand. The bonding in these complexes has been investigated by a combination of crystallographic and computational techniques. Sb–Pd bonding has been characterized as dative, with the largest component of electron density remaining localized at Sb. The Lewis amphotericism of the chlorostibine ligands gives rise to secondary Sb...Cl bonds, observed in the solid state of all complexes, arising from $\text{lp}_{\text{Cl}} \rightarrow \text{Sb } \sigma_{\text{Sb-Cl}}^*$ interactions. In compounds 1–4, this secondary bonding drives the formation of supramolecular structures, including two dimers, a tetramer, and a polymer. The square-pyramidal Pd(II) complex **5** is an unprecedented example of PdSb₅ coordination, in which the fifth axial ligand coordinates via a $\text{lp}_{\text{Sb}} \rightarrow \text{Pd } \sigma_{\text{Pd-Sb}}^*$ donor–acceptor interaction.

EXPERIMENTAL SECTION

Preparations were undertaken using standard Schlenk and glovebox techniques under a N₂ atmosphere. Solvents were dried using a solvent purification system (MBraun SPS 800; toluene, CH₂Cl₂, Et₂O, *n*-hexane) or distillation over sodium wire (benzene) and degassed with N₂ prior to use. [PdCl₂(MeCN)₂] was prepared by refluxing PdCl₂ in MeCN. SbMe₂Cl was prepared by a modification of the literature method.³¹ ¹H and ¹³C{¹H} NMR spectra were recorded using a JEOL Eclipse 400 MHz spectrometer at ambient temperature (25 °C) and are referenced to the residual solvent signal. The purity of the compounds was established by microanalysis on crystalline samples where possible. Microanalyses were performed by London Metropolitan University.

[Pd₄Cl₈(SbMe₂Cl)₄] (1). To a stirring suspension of [PdCl₂(MeCN)₂] (0.121 g, 0.466 mmol) in toluene (10 cm³) was added a solution of SbMe₂Cl (0.47 mmol, 1 equiv) in toluene (3 cm³), giving a deep-green suspension that rapidly became red-brown. After being stirred at room temperature for 4 days, the dark red-brown product was collected by filtration, washed with hexane (10 cm³), and dried in vacuo. Yield: 0.110 g (0.075 mmol, 65%). Large red-black crystals suitable for X-ray diffraction were obtained by dissolving ca. 50 mg of this compound in boiling THF (15 cm³), concentrating the solution in vacuo to ca. 50% of its original volume, and overlaying with hexane (40 cm³). ¹H NMR (400 MHz, CDCl₃, 293 K): δ 2.22 (24H, s, (H₃C)₂Sb). Anal. Calcd for C₈H₂₄Cl₁₂Pd₄Sb₄ (%): C, 6.59; H, 1.66. Found: C, 7.19; H, 1.49.

[Pd₂Cl₄(SbMe₂Cl)₄] (2) and Crystals of [Pd₂(SbMe₂Cl)₈]Cl₄ (4). A solution of SbMe₂Cl (2.92 mmol, 2 equiv) in toluene (35 cm³) was added directly to solid [PdCl₂(MeCN)₂] (0.373 g, 1.440 mmol), giving a yellow suspension that turned bright-red after ca. 2 h. After being stirred at room temperature for 2 days, the bright-red product was collected by filtration, washed with Et₂O, and dried in vacuo. Yield: 0.502 g (0.455 mmol, 63%). ¹H NMR (400 MHz, CD₂Cl₂, 293 K): δ 2.22 (24H, s, (H₃C)₂Sb). ¹³C NMR (100 MHz, CDCl₃, 293 K): δ 16.3 ((H₃C)₂Sb) Altering the procedure so that after the first 2 h stirring was stopped and the solution was allowed to stand for a few days yielded red prisms of **2** with the previously reported structure.¹⁷ Recrystallization of the product from CH₂Cl₂ at −18 °C gave rod-shaped crystals of the solvate 2·2CH₂Cl₂. Recrystallization of the

product from benzene at room temperature gave a few crystals of the solvate 2·4C₆H₆. On one occasion, after the product was collected, the remaining toluene/Et₂O filtrate was concentrated in vacuo until a yellow solid began to precipitate. Heating the mixture to boiling caused this to redissolve, furnishing an orange solution, which upon cooling to −18 °C became deep-green in color. After storage for 3 days at −18 °C, a microcrystalline yellow solid formed. X-ray diffraction analysis (poor quality data) revealed this to be 4.

[PdCl(SbMe₂Cl)₂(SbMe₂Cl₂)] (3). A solution of SbMe₂Cl (0.44 mmol, 3 equiv) in toluene (10 cm³) was added to a stirring suspension of [PdCl₂(MeCN)₂] (0.038 g, 0.147 mmol) in toluene (10 cm³), rapidly forming a bright orange-brown solution that began to deposit solid after ca. 15 min. After being stirred at room temperature for 2 days, the mixture was concentrated in vacuo to ca. 50% of its original volume, then the orange-yellow product was collected by filtration, washed with hexane (30 cm³), and dried in vacuo. Yield: 0.051 g (0.069 mmol, 47%). ¹H NMR (400 MHz, CDCl₃, 293 K): δ 2.13 (18H, s, (H₃C)₂Sb). ¹³C NMR (100 MHz, CDCl₃, 293 K): δ 16.27 ((H₃C)₂Sb). ¹H NMR (400 MHz, CD₂Cl₂, 293 K): δ 2.11 (18H, s, (H₃C)₂Sb). ¹³C NMR (100 MHz, CD₂Cl₂, 293 K): δ 17.16 ((H₃C)₂Sb). Anal. Calcd for C₆H₁₈Cl₃PdSb₃ (%): C, 9.75; H, 2.45. Found: C, 9.82; H, 2.44. Large golden-yellow crystals suitable for X-ray diffraction were obtained via slow diffusion of the layered toluene/hexane filtrate at room temperature.

[Pd(SbMe₂Cl)₃]Cl₂ (5). A solution of SbMe₂Cl (2.02 mmol, 4.2 equiv) in toluene (10 cm³) was added to a stirring suspension of [PdCl₂(MeCN)₂] (0.126 g, 0.4860 mmol) in toluene (10 cm³), giving a suspension that was briefly deep-green in color, rapidly turning bright yellow. After being stirred at room temperature, the yellow product was collected by filtration, washed with hexane (30 cm³), and dried in vacuo, during which it was observed to darken slightly. Yield: 0.251 g. ¹H NMR (400 MHz, CDCl₃, 293 K): δ 2.11 (48H, s, (H₃C)₂Sb). ¹³C NMR (100 MHz, CDCl₃, 293 K): δ 16.47 ((H₃C)₂Sb). Recrystallization from this solid gave crystals of 3 only. Anal. Calcd for 3 C₆H₁₈Cl₃PdSb₃ (%): C, 9.75; H, 2.45; for 4 C₁₆H₄₈Cl₁₂Pd₂Sb₈: C, 10.37; H, 2.61; for 5 C₁₀H₃₀Cl₇PdSb₅: C, 10.78; H, 2.72. Found: C, 10.52; H, 2.34. Cooling the layered toluene/hexane filtrate to −18 °C caused the toluene layer to rapidly change color from yellow to deep-green, and after storage at −18 °C for 3 days, a few large, very dark green crystals formed. These were determined by X-ray crystallography to be [Pd(SbMe₂Cl)₃]Cl₂. Warming of the solution returned it to a yellow color. Repeating the experiment with up to 5.5 equiv of SbMe₂Cl gave very similar results.

Attempted Direct Preparation of 4, Resulting in Decomposition to 3. A solution of SbMe₂Cl (1.82 mmol, 4 equiv) in toluene (10 cm³) was added directly to solid [PdCl₂(MeCN)₂] (0.117 g, 0.451 mmol), giving a deep-green suspension that turned bright-yellow within a few minutes. After being stirred at room temperature for 1 day, the lemon-yellow product was collected by filtration and washed with Et₂O (10 cm³). After being dried in vacuo, a slight darkening to orange-yellow was observed. Powder XRD of the dried product matched that predicted for complex 3, with no other phases identified. Yield: 0.254 g (0.344 mmol, 76% vs Pd). Anal. Calcd for C₆H₁₈Cl₃PdSb₃ (%): C, 9.75; H, 2.45. Found: C, 9.89; H, 2.22.

Computational Methods. Unconstrained geometry optimizations and subsequent frequency calculations of all complexes were carried out at the DFT level using ORCA 4.0.0.2.³² These calculations employed the BP86 GGA functional^{33,34} in conjunction with the RI-J approximation.^{35–37} The def2-TZVP basis set was used on all atoms,³⁷ combined with the corresponding Weigend *J* auxiliary basis.^{38,39} Core electrons of heavier elements (Pd,⁴⁰ Sb⁴¹) were replaced by the appropriate relativistic def2-ECP effective core potentials. Dispersion effects were accounted for by including Grimme's DFT-D3 method in combination with Becke–Johnson damping (D3BJ).^{42,43} Stationary points were confirmed to be minima by the absence of imaginary frequencies. The electronic structure of the complexes was analyzed by means of localized molecular orbitals, generated with the Pipek–Mezey method,⁴⁴ and natural bond orbitals

(NBO6).⁴⁵ These calculations utilized both the ORCA 4.0.0.2 and Gaussian09 (rev D.01) software,⁴⁶ employing the same level of theory as described above to calculate the required wave functions on the DFT-optimized geometries.

Crystallographic Methods. Data collections were carried out using either an Oxford Xcalibur Gemini diffractometer equipped with a Sapphire3 CCD detector at a temperature of 100 K or a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector at a temperature of 150 K. Refinement details and crystallographic parameters can be found in the [Supporting Information](#).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.organomet.8b00556](https://doi.org/10.1021/acs.organomet.8b00556).

Detailed computational information, crystallographic information, UV–vis spectra, NMR spectra, photographs of reaction solutions (PDF)

Structure coordinates (XYZ)

Accession Codes

CCDC 1853471–1853475 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was partially funded by EPSRC Grant EP/R020418/1. We thank Prof. Stuart A. Macgregor (Heriot-Watt University) for providing access to high-performance computing facilities. We also thank Prof. W. Levason and Prof. G. Reid (University of Southampton) for helpful discussions.

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