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Trivalent Antimony as L-, X-, and Z-Type Ligand: The Full Set of Possible Coordination Modes in Pt–Sb Bonds

Erik Wächtler, Robert Gericke, Theresa Block, Rainer Pöttgen, and Jörg Wagler*

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ABSTRACT: In the course of our investigations of the coordination chemistry of trivalent antimony (Sb) compounds, we studied heteronuclear complexes formed in reactions of the compounds $RSb(pyS)_2$ (R = pyS, Ph; pyS⁻ = pyridine-2-thiolate) with $[Pt(PPh_3)_4]$, i.e., complexes $[(R)Sb(\mu-pyS)_2Pt-(PPh_3)]$ (R = pyS, 1; R = Ph, 2). The reaction of 1 with *o*-chloranil proceeds cleanly with elimination of 2,2'-dipyridyl disulfide and formation of the salt $[(PPh_3)Pt(\mu-pyS)_2Sb(\mu-pyS)_2Pt(PPh_3)]^+[Sb(C_6Cl_4O_2)_2]^-$ (3^{III}), which features the cation 3⁺. The charge-neutral, unsymmetrically substituted compound $[(PPh_3)Pt(\mu-pyS)_2Sb(\mu-pyS)_2Pt(KS-pyS)]$ (4) can be accessed by the reaction of 3⁺ with LipyS. The oxidation of 2 with *o*-chloranil furnishes the complex $[(\kappa-O,O-C_6Cl_4O_2)PhSb(\mu-pyS)_2Pt(PPh_3)]$ (5). The oxidation of 1 with PhICl₂ afforded the paddlewheel-shaped complex $[Sb(\mu-pyS)_4PtCl]$ (6). Moreover, compound 6 was obtained by the reaction of Sb(pyS)₃ with $[PtCl(pyS)-(PPh_3)]$. The polarization of Pt-Sb bonds of compounds 1–6 was investigated



by natural localized molecular orbital (NLMO) calculations, which suggest X-type ligand character (covalent Pt–Sb bonds) for 1 and 2, whereas the Sb ligand of 6 reflects Z-type character (dative Pt \rightarrow Sb bonds). In 3⁺, 4, and 5, high contributions of the reverse, i.e., L-type (dative Pt \leftarrow Sb bonds), were observed. In conjunction with the results of NLMO analyses, ¹²¹Sb Mössbauer spectroscopy proves that complexes 1–6 represent essentially trivalent Sb complexes with either a free lone pair (LP) at the Sb atom (1, 2, and 6) or LP character involved in L-type Pt \leftarrow Sb coordination (3⁺, 4, and 5).

INTRODUCTION

In the past decade, a variety of heterobimetallic complexes, which combine antimony [Sb, as well as bismuth (Bi)] and late transition metals (TMs), have been shown to reveal very interesting coordination features.¹⁻⁷ Both because of the versatility of coordination modes of the TM-Sb (Bi) bond and also in terms of their unique redox chemistry, the heavy pnictogen ligand moieties of these compounds can be regarded as a distinct ligand class. Gabbaï, who pioneered work in this field, introduced the term σ -donor/acceptor-confused ligands.⁸ For instance, the compounds $R'Sb(C_6H_4PR''_2)_2$ (R' = Cl, $C_6H_4PPh_2$; R" = Ph, *i*Pr) display entirely different coordinations toward AuCl: For R' = aryl and R'' = Ph, L-type (Lewis base) coordination can be observed,² whereas for R' = Cl and R'' = iPr, the trivalent Sb compound acts as a Z-type ligand (Lewis acid;⁸ Chart 1, I and II). All three possible coordination modes of Sb toward a TM (including X-type coordination) have been observed in a set of complexes with a Ni/Sb core, but in this case, oxidation from the trivalent Sb (L-type; III in Chart 1) to the pentavalent state of Sb was crucial for realization of the X-type (IV) or Z-type (V) coordination modes.⁹ Considering the diverse Lewis acidic/basic behavior of trivalent Sb compounds,¹⁰ all three (L-, X-, and Z-type) coordination modes should in general also be possible for trivalent Sb compounds, i.e., compounds bearing a lone pair

(LP) at the Sb atom (either free or involved in Sb \rightarrow TM L-type bonding). To the best of our knowledge, this has not been reported so far for a series of complexes related to one another.

Recently, it was shown that delocalization of the negative charge in the pyridine-2-thiolate ligand leads to bonding in heterobimetallic tin (Sn)/[nickel (Ni), palladium (Pd), platinum (Pt)] compounds, the interpretation of which is rather ambiguous (i.e., diverse L-, X-, and Z-type), and therefore a closer inspection of the Sn–TM bond (its polarization toward Sn or TM) was crucial for the interpretation.^{11–14} Furthermore, we have reported on a complex (VI) with a pyridine-2-thiolate-bridged rhodium (Rh)/Sb core featuring a trivalent Sb ligand and a short Rh–Sb bond. Its oxidation afforded complex VII. Whereas one may straightforwardly assign a pentavalent Sb atom in VII, the analytical results revealed an ambiguous bonding situation, also featuring an Sb→Rh bond (i.e., trivalent Sb has to be

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Chart 1. Complexes I–VII Featuring Selected Tri- and Pentavalent Sb Ligands in the Coordination Sphere of Late TMs and Scope of This Paper



Scheme 1. Syntheses of Complexes $1-6^a$



^{*a*}For the salts of cation 3^+ , obtained in deliberate syntheses, the compound numbers 3^{III} and 3^V are used for $3[Sb(C_6Cl_4O_2)_2]$ and $3[Sb(C_6Cl_4O_2)_3]$, respectively.

considered for VII as well).¹⁵ Herein, we now report on a series of heterometallic Pt/Sb complexes for which natural localized molecular orbital (NLMO) analyses suggest distinct

Pt←Sb (L-type), Pt−Sb (X-type), and Pt→Sb (Z-type) bonds. In conjunction with ¹²¹Sb Mössbauer spectroscopy, those complexes are shown to inevitably represent trivalent Sb

В

compounds (together with one ambiguous bonding situation analogous to VII).

RESULTS AND DISCUSSION

Syntheses. While our previously reported Rh/Sb complexes¹⁵ combined Sb with a potential d^8/d^6 system, we were aiming at the synthesis of Pt/Sb complexes by the reaction of Sb(pyS)₃¹⁶ with low-valent Pt compounds, thus equipping the heteronuclear complexes with a d^{10}/d^8 TM. Indeed, the reaction of Sb(pyS)₃ with [Pt(PPh₃)₄] in tetrahydrofuran (THF) afforded the complex [(κ S-pyS)Sb(μ -pyS)₂Pt(PPh₃)] (1) in good yield (Scheme 1). Moreover, analogous synthesis starting from compounds PhSb(pyS)₂¹⁷ and [Pt(PPh₃)₄] furnished [PhSb(μ -pyS)₂Pt(PPh₃)] (2).

The molecular structures of 1 and 2 were determined by X-ray crystallography (Figure 1). Both molecules feature short



Figure 1. Molecular structures of 1 and 2 in the crystal structures of 1.2THF and 2. Ellipsoids set at 50% probability. H atoms and solvent of crystallization are omitted for clarity. Selected bond lengths (Å) and angles (deg) for 1: Pt1–Sb1 2.5749(4), Pt1–S1 2.311(1), Pt1–S2 2.307(1), Pt1–P1 2.362(1), Sb1–N1 2.412(5), Sb1–N2 2.308(5), Sb1–S3 2.466(2), Sb1…N3 3.323(5); S1–Pt1–S2 174.52(5), Sb1–Pt1–P1 174.85(3), N1–Sb1–N2 164.8(2), S3–Sb1–Pt1 100.32(4). Selected bond lengths (Å) and angles (deg) for 2: Pt1–Sb1 2.5878(2), Pt1–S1 2.3078(7), Pt1–S2 2.3035(7), Pt1–P1 2.3660(7), Sb1–N1 2.355(2), Sb1–N2 2.373(2), Sb1–C11 2.179(3); S1–Pt1–S2 176.36(3), Sb1–Pt1–P1 169.63(2), N1–Sb1–N2 167.05(8), C11–Sb1–Pt1 102.96(8).

Pt-Sb bonds (1, 2.57 Å; 2, 2.59 Å). The Pt atoms adopt square-planar coordination geometry. The seesaw coordination about Sb is indicative of the presence of an Sb-located LP (:ER₄-type according to valence-shell electron-pair repulsion theory). The Pt-S [approximately (ap.) 2.31 Å] and Pt-P (ap. 2.36 Å) bonds of 1 and 2 are similar. The Sb-N bonds of 1 are quite different (2.31 and 2.41 Å) but, on average (av.), similar to those found in 2 (2.36 and 2.37 Å). The Sb...N separation, which involves the κ S-bound pyS moiety of 1 (3.32) Å), is, because of the higher coordination number (CN) of Sb in 1 (CN = 4), significantly longer than that in $Sb(pyS)_3$ (2.84 Å; CN = 3).¹⁶ Hence, additional coordination ([4 + 1] coordination) by the N atom of the otherwise dangling pyS ligand is only marginal. As a result, the S-Sb-Pt angle of 1 (100°) is similar to the C-Sb-Pt angle in 2 (103°). The ¹H and ${}^{13}C{}^{1}H$ NMR spectra of 1 and 2 in solution are well in agreement with the molecular structures found by X-ray diffraction in the solid state (two sets of resonances for the different pyS ligands in 1 in a 1:2 ratio and one set of signals of the two bridging pyS ligands in **2**). The ${}^{31}P{}^{1}H{}$ NMR spectra feature resonances at 34.7 ppm (1) and 32.7 ppm (2), flanked by Pt satellites (${}^{1}J_{Pt-P}$ = 2226 and 2201 Hz, respectively) of couplings that are smaller than those in our previously reported complex $[Cl_2Sn(\mu-pyS)_2Pt(PPh_3)]$ (trans-Sn-Pt-P, 3330

Hz).¹³ Those weaker couplings are in accordance with the longer Pt–P bonds for 1 (2.36 Å) and 2 (2.37 Å) compared to the Pt/Sn complex (2.33 Å).¹⁸

The treatment of 1 with o-chloranil as an oxidizing agent in a 1:1 molar ratio (in a toluene solution) proceeds cleanly, but unexpectedly, with the formation of 2,2'-dipyridyl disulfide (pyS-Spy) and the salt $[(PPh_3)Pt(\mu-pyS)_2Sb(\mu-pyS)_2Pt (PPh_3)^{+}$ [Sb(C₆Cl₄O₂)₂]⁻ (3^{III}; Scheme 1). In this reaction, four electrons are required for the reduction of 2 equiv of ochloranil to the catecholate ligand in the Sb^{+III} anion of 3^{III}. Hence, the formation of 3^{III} out of 2 equiv of 1 is accompanied by a two-electron oxidation of the metal core and the oxidation of two of the pyS ligands (pyS⁻ anions) to the disulfide (for details, see below). The use of excess of o-chloranil leads to further oxidation of the Sb^{+III} anion of 3^{III} to Sb(C₆Cl₄O₂)₃⁻. The salt 3^{V} featuring this Sb^{+V} anion was isolated as a pure compound by the reaction of 1 with 1.5 equiv of o-chloranil. (Denotations as 3^{III} and 3^{V} are used for compounds featuring the Sb^{+III} or Sb^{+V} anion, respectively, as well as 3^+ for the cation.) The structures of both 3^{III} and 3^{V} were determined by single-crystal X-ray diffraction, and the data of 3^V are included in the discussion (see the Supporting Information for related metrical parameters of 3^+ in 3^{111} , which are essentially equal to those in 3^{V}). Furthermore, the treatment of 3^{V} with LipvS in a 1:1 molar ratio replaces one of the PPh₃ ligands of 3^+ with formation of the neutral complex $[(PPh_3)Pt(\mu-pyS)_2Sb(\mu$ $pyS)_2Pt(\kappa S-pyS)$ (4; Scheme 1), which was obtained as a solid of very poor solubility. The identity of this compound was confirmed by solid-state ³¹P NMR spectroscopy and single-crystal X-ray structure analysis. (For the latter, single crystals of this hardly soluble compound were grown by layering the starting materials with THF.) Upon storage at room temperature, coarse crystalline single crystals of 4 formed and were isolated from the reaction mixture (see Figure 2 for the structures of 3^+ and 4). The rather poor yield of 21% can be due to the loss of product during decantation of the mother liquor, which was accompanied by removal of the turbidities and product of smaller crystal size. For the synthesis of 4, excess LipyS has to be avoided because of the potential risk of formation of the 2-fold-substituted complex $[(\kappa S-pyS)Pt(\mu$ $pyS)_2Sb(\mu-pyS)_2Pt(\mu-pyS)Li(THF)_3$ (4[#]) and also of the Pt^{+II} complex $[Pt(pyS)_2(PPh_3)_2]$ (see the Supporting Information for details). The molecular composition of 4 allows for the conclusion that its synthesis can be achieved by the reaction of 1 with $[Pt_2(pyS)_4]$ or $[Pt(pyS)_2(PPh_3)_2]$. However, in both cases, no reaction of the starting materials was observed, probably because of the relatively high stability of these Pt+II compounds (coordinatively saturated with ligands of good σ -LP donor quality).

There is a close structural analogy of 3^+ to the Sn complex $[(PPh_3)Pd(\mu-pyS)_2Sn(\mu-pyS)_2Pd(PPh_3)]$, which we have reported earlier.¹² The Sb atoms of 3^+ and 4 are surrounded by four N and two Pt atoms (Pt trans) in a distorted octahedral fashion, and the Pt atoms are located in square-planar coordination environments. The Pt–Sb bond lengths of 3^+ (2.57 and 2.58 Å) are similar to those found in 1 and 2. In 4, two rather different Pt–Sb bond lengths are observed (Pt2–Sb1, 2.53 Å, Pt1–Sb1, 2.59 Å) with the shorter bond trans to the κ S-bound pyS ligand. Similarly, the Pt2–S3/4 bonds (2.28 and 2.28 Å) are notably shorter than the Pt1–S1/2 bonds (2.30 and 2.31 Å). Both 3^+ and 4 reveal rather different Sb–N bond lengths (ranging between 2.26 and 2.59 Å), in both cases as pairs of a shorter and a longer Sb–N bond trans-disposed.



Figure 2. Molecular structures of 3^+ and 4 in the crystal structures of 3^V·DCM and 4·3THF. Ellipsoids set at 50% probability. H atoms and solvent of crystallization omitted for clarity. Selected bond lengths (Å) and angles (deg) for 3+: Pt1-Sb1 2.5751(2), Pt2-Sb1 2.5713(2), Pt1-S1 2.2986(6), Pt1-S2 2.3145(7), Pt2-S3 2.2927(6), Pt2-S4 2.3141(6), Pt1-P1 2.3248(6), Pt2-P2 2.3302(6), Sb1-N1 2.586(2), Sb1-N2 2.255(2), Sb1-N3 2.397(2), Sb1-N4 2.311(2); Pt1-Sb1-Pt2 168.525(7), N1-Sb1-N2 167.48(7), N3-Sb1-N4 166.40(8), S1-Pt1-S2 173.23(3), S3-Pt2-S4 172.71(2). Selected bond lengths (Å) and angles (deg) for 4: Pt1-Sb1 2.5890(6), Pt2-Sb1 2.5275(6), Pt1-S1 2.311(2), Pt1-S2 2.295(2), Pt2-S3 2.284(2), Pt2-S4 2.284(2), Pt1-P1 2.332(2), Pt2-S5 2.368(2), Sb1-N1 2.500(6), Sb1-N2 2.287(6), Sb1-N3 2.464(6), Sb1-N4 2.295(6); Pt1-Sb1-Pt2 172.22(2), N1-Sb1-N2 170.7(2), N3-Sb1-N4 173.5(2), S1-Pt1-S2 174.39(7), S3-Pt2-S4 170.51(7).

Because of the octahedral coordination of Sb in 3^+ and 4 (CN = 6), the average Sb–N bond lengths (3^+ , 2.38 Å; 4, 2.39 Å) are slightly longer than those in 1 and 2 (seesaw coordination, 2.36 Å each). The ¹H and ¹³C{¹H} NMR spectra of 3^V in solution are in agreement with the molecular structure observed in the solid state (equivalent pyS and PPh₃ ligands).

The ³¹P{¹H} NMR spectrum of **3**^V (Figure 3) reveals an interesting coupling pattern of the signal centered at 28.4 ppm. This pattern arises from the natural abundance of the NMR-active ¹⁹⁵Pt isotope (34%), in conjunction with the presence of two chemically equivalent Pt–P motifs. A ³¹P NMR signal with a similar pattern has been reported for the complex [Pt(μ -Ph₂Ppy)Cl]₂.¹⁹ The most striking feature of this pattern, however, is the ⁴J_{P-P} coupling of 47 Hz that can be extracted from the spectrum. This ⁴J_{P-P} interaction is indicative for a strong electronic interaction across the trimetallic Pt–Sb–Pt core. Moreover, the ²J_{Pt-Pt} coupling can be estimated to about 960 Hz. (A detailed description of the occurrence of the signal pattern is given in the Supporting Information.)

Whereas the oxidation of 1 with o-chloranil resulted in the elimination of (pyS)₂ and formation of the trinuclear Pt-Sb-Pt core, an analogous reaction of 2 with 1 equiv of o-chloranil furnishes the compound $[(\kappa - O_1O - C_6Cl_4O_2)PhSb(\mu - pyS)_2Pt (PPh_3)$ (5), in accordance with the expected formal twoelectron oxidation at Sb (Scheme 1).²⁰ The formation of 3^{III} with the elimination of biphenyl was not observed. The oxidation of compound 1 with PhICl₂ also gave the cationic complex 3^+ (probably as SbCl₄⁻ salt), as can be derived by observation of the characteristic ³¹P NMR signal of this complex in the crude reaction mixture. Moreover, also (pyS)₂ was detected in the ¹H NMR spectrum of the same mixture. Upon storage at room temperature, however, the paddlewheel-shaped complex $[Sb(\mu-pyS)_4PtCl]$ (6; Scheme 1) crystallized within 2 days and was isolated in 26% yield.²¹ Along an alternative route, which seems to be a more deliberate synthesis, starting from Sb(pyS)₃ and [PtCl(pyS)-(PPh₃)], we obtained compound 6 (which crystallized from this reaction mixture as a poorly soluble complex) in 13% yield only. The formation of 6 competes with the ligand-exchange process to give $ClSb(pyS)_2$ and $[Pt(pyS)_2(PPh_3)]$, the latter of which was identified by ${}^{31}P{}^{1}H$ NMR spectroscopy of the crude reaction mixture ($\delta_{31P} = 7.3 \text{ ppm}; {}^{1}J_{Pt-P} = 3870 \text{ Hz}$),²² and thus serves as an explanation for the unexpectedly poor yield of 6. The molecular structures of 5 and 6 are depicted in Figure 4.

The Sb atom of **5** is octahedrally coordinated. Because of the presence of two-electronegative O atoms in the coordination sphere of Sb, the Sb–N (av. 2.25 Å), Sb–C (2.16 Å), and Pt–Sb (2.53 Å) bond lengths are significantly shorter than the corresponding bonds in **2** (2.36, 2.18, and 2.59 Å, respectively), which is the most striking difference between the related structural fragments of **2** and **5**. The Sb–O bond



Figure 3. ${}^{31}P{}^{1}H$ NMR spectrum of 3^V in CD₂Cl₂.

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Figure 4. Molecular structures of 5 (30% ellipsoids) and 6 (50% ellipsoids). H atoms omitted for clarity. Selected bond lengths (Å) and angles (deg) for 5: Pt1–Sb1 2.5266(7), Pt1–S1 2.293(3), Pt1–S2 2.293(3), Pt1–P1 2.311(2), Sb1–N1 2.261(8), Sb1–N2 2.240(8), Sb1–C11 2.16(1), Sb1–O1 2.035(6), Sb1–O2 2.125(7); S1–Pt1–S2 174.8(2), Sb1–Pt1–P1 174.17(7), N1–Sb1–N2 169.6(3), O1–Sb1–Pt1 168.9(2), O2–Sb1–C11 160.94, C11–Sb1–Pt1 108.0(3). Selected bond lengths (Å) and angles (deg) for 6: Pt1–Sb1 2.5519(2), Pt1–S1 2.3513(8), Pt1–S2 2.3475(7), Pt1–S3 2.3599(7), Pt1–S4 2.3522(7), Pt1–Cl1 2.4996(7), Sb1–N1 2.368(3), Sb1–N2 2.339(2), Sb1–N3 2.329(2), Sb1–N4 2.487(3); S1–Pt1–S3 175.61(3), S2–Pt1–S4 172.26(3), Sb1–Pt1–Cl1 178.41(2), N1–Sb1–N3 161.7(1), N2–Sb1–N4 169.88(8).

lengths (trans-Pt, 2.04; cis-Pt, 2.13 Å) are comparable to those found in the Sb^{+III} anion Sb(C₆Cl₄O₂)₂⁻ and longer than those in $Sb(C_6Cl_4O_2)_3^-$ (Sb^{+V}; see the Supporting Information). Also, the Pt–P bond length in 5 (2.31 Å) is shorter than that in 2 (2.37 Å), which is also reflected in the larger ${}^{1}J_{\text{Pt-P}}$ coupling constant of 5 (3067 Hz) compared to that of 2 (2201 Hz; see the discussion for complexes 1 and 2 and the Pt/Sn complex above together with ref 18). Unexpectedly, the C-Sb–Pt angle in 5 (108°) is wider than that in 2 (103°), which might be due to an attractive contact between an O atom of the catecholate ligand and one of the SbPh_{ortho} protons. Complex 6 is electronically related to paddle-wheel-shaped complexes of the type $[XSi/Sn(\mu-mt)_4Ni/Pd/PtX']$ (mt = 2methimazolyl),²³ considering the formal substitution of X–Si/ Sn for Sb. Whereas the latter were found to exhibit nearly perfect paddle-wheel motifs (four similar Si/Sn-N bonds and four similar Ni/Pd/Pt-S bonds), the molecular structure of 6 reveals one longer Sb–N bond (2.49 Å) compared to the other Sb–N bonds (2.33–2.37 Å). The av. Sb–N distance (2.38 Å), however, is similar to those found in 3 (av. 2.38 Å) and 4 (av. 2.39 Å). Whereas the cis-N-Sb-N bond angles between the shorter Sb–N bonds are smaller than 90°, one N–Sb–N angle adjacent to the long Sb-N bond is wider than 100°, thus indicating some influence of the Sb-located LP into this direction. Because of hexacoordination of the Pt atom in 6, the Pt-S distances are longer than those in 1-5, which feature tetracoordinate Pt. The poor solubility of 6 in organic solvents only allows for the observation of ¹H (not ¹³C) NMR signals, which indicate the equivalency of the pyS ligands in solution.

¹²¹Sb Mössbauer Spectroscopy. Although the ¹²¹Sb Mössbauer isomer shift (δ) of an Sb compound strongly depends on the substitution pattern of the Sb atom (i.e., δ values of both trivalent and pentavalent Sb compounds cover wide ranges), this method represents the most powerful tool for the distinction between the two valence states of Sb (trivalent Sb compounds of roughly $\delta < -6 \text{ mm s}^{-1}$ and pentavalent of $\delta > -6 \text{ mm s}^{-1}$, relative to Ba^{121m}SnO₃).²⁴ Arylantimony compounds exhibit δ values close to this threshold, with the least negative values for the formal trivalent Sb compounds observed for triorganostibines coordinated

toward a TM (pentavalent, $Ph_3SbCl_2^{25}$ -6.02 mm s⁻¹; metal-coordinated trivalent, $[PtCl_2(SbPh_3)_2]^{26}$ -6.44 mm s⁻¹). Sb compounds with a higher degree of ionic bonding (i.e., featuring more electronegative substituents) exhibit pronounced differences of δ values between related trivalent and pentavalent Sb compounds (pentavalent, Sb₂O₅ ca. 0 mm s⁻¹; trivalent, Sb₂O₃ ca. -11 mm s⁻¹).²⁷ In general, the isomer shift differences mainly arise from different 5s orbital populations. Therefore, pronounced negative shifts reflect high 5s orbital occupancy, i.e., the presence of an Sb-located LP with a high degree of 5s orbital character. In order to classify complexes 1-6 with respect to the electronic situation of their Sb atoms. we have recorded their ¹²¹Sb Mössbauer spectra. Because of the low isolable amounts of 4, the spectrum of this complex, however, could not be obtained because ¹²¹Sb Mössbauer spectroscopy requires relatively large amounts of sample. In order to obtain the δ value of the Sb atom in 3⁺, we have chosen complex 3^{V} (not 3^{III}) because the signal of the Sb^{+V} anion was expected not to overlap with the signal of the cation. Moreover, we have included the ¹²¹Sb Mössbauer spectrum of $Sb(pyS)_3$ (as a trivalent Sb reference).¹⁵ Furthermore, as benchmark compounds for TM- and pyS-containing Sb complexes, we include the Mössbauer parameters of the Rh/ Sb complex VI and its oxide VII from our previous study in the current discussion (see Table 1 for spectroscopic parameters of

Table 1. Parameters of the Fitting Procedure of the ¹²¹Sb Mössbauer Spectra at 5 K: Isomer Shift δ (mm s⁻¹) Relative to Ba^{121m}SnO₃, Electronic Quadrupole Interaction eQV_{zz} (mm s⁻¹), Experimental Line Width Γ (mm s⁻¹), and Asymmetry Parameter η

	δ	eQV _{zz}	Г	η
1	-12.39(3)	15.7(2)	2.84(7)	0.44(3)
2	-11.19(3)	-14.6(2)	2.47(6)	0.93(3)
3+	-10.28(4)	18.1(3)	2.5(1)	0.17(4)
$Sb(C_6Cl_4O_2)_3^-$	-0.67(4)	-3.2(4)	2.3(1)	
5	-6.02(3)	-8.9(1)	2.89(7)	0.98(4)
6	-14.52(3)	14.2(1)	2.51(6)	
VI	-13.2(1)	17.8(2)	3.1(1)	0.29(3)
VII	-6.9(1)	11.3(1)	2.9(1)	0.31(3)
Sb(pyS) ₃	-13.9(1)	6.0(2)	2.7(1)	0.3(1)

all complexes discussed herein). The spectra of 1-6 (except of 4) and Sb(pyS)₃ (reference, starting material for the synthesis of 1) are depicted in Figure 5.

As anticipated from the coordination geometry of the Sb atom of 1 and 2 (seesaw coordination, LP at Sb), complexes 1 $(-12.4 \text{ mm s}^{-1})$ and 2 $(-11.2 \text{ mm s}^{-1})$ feature δ values similar to that of $Sb(pyS)_{3}$ ¹⁵ i.e., in the typical range of trivalent Sb complexes. Compared to complex VI (four electronegative N atoms in one plane), the different pyS coordinations of Sb in 1 and 2 (two N atoms and one S atom) with fewer electronegative atoms lead to a slightly less negative δ and a significantly smaller electronic quadrupole interaction (eQV_{zz}: 1, 16 mm s⁻¹; 2, -15 mm s⁻¹), with the latter indicating a more symmetric electronic distribution around Sb in 1 and 2. Thanks to the unsymmetrical quadrupole splitting of the ¹²¹Sb Mössbauer signals (different intensities of the lines), the sign of the electric field gradient tensor and the electronic quadrupole interaction, respectively, can be extracted from the spectrum. Hence, the different relative orientations of the signals of 1 and 2 are caused by different signs of eQV_{zz} . Complex 3^V reveals a



Figure 5. Experimental (dots) and simulated (lines) ¹²¹Sb Mössbauer spectra of complexes Sb(pyS)₃ (taken from ref 15), **1**, **2**, **3**^V, **5**, and **6**, relative to Ba^{121m}SnO₃ at 5 K. Vertical line plotted at -10 mm s^{-1} for sake of better comparability. For **3**^V, cyan line for the **3**⁺ cation and green line for the Sb(C₆Cl₄O₂)₃⁻ anion.

Table 2. NLMO Characteristics of the Pt–Sb Bond (BD Pt–Sb) and LPs at Sb (LP Sb) with 5s/5p (for Sb), and 6s/5d (for Pt) Orbital Contributions to these NLMOs

	1	2	3 ^{+ a}	4	5	6
% BD(Pt-Sb)	94	94	94	86	92	72 ^b
% Sb (5s, 5p)	47 (12/88)	47 (14/86)	61 (54/46)	52 (7/93)	55 (62/38)	22 (14/86)
% Pt (6s, 5d)	49 (33/67)	49 (31/69)	35 (36/64)	37 (30/70)	41 (34/65)	73 (2/98)
% LP(Sb)	98	98		78		98
% Sb (5s, 5p)	98 (82/18)	98 (76/24)		80 (94/6) ^c		98 (85/15)

"Average of two similar NLMOs. ^bNLMO treats the Pt–Sb bond for **6** as LP(Pt). ^cFurther contribution of the Pt(κ S-pyS) moiety to this NLMO: 9% Pt (6s 42%, 5d 56%); 6% S (3s 10%, 3p 90%).



Figure 6. Plots of selected NLMOs (isosurface value of 0.05) of compounds 1–6. Atom color codes: purple, Sb; cyan, Pt; blue, N; yellow, S; brown, P; green, Cl; red, O; gray, C.

sharp signal at -0.7 mm s^{-1} , which arises from the Sb^{+V} anion. The signal of the 3⁺ cation, which covers a wide range with eQV_{zz} of 18.2 mm s⁻¹ (similar to VI), appears well separated at $\delta = -10.3 \text{ mm s}^{-1}$. Interestingly, this suggests a trivalent state for Sb in 3⁺, i.e., LP characteristics at Sb. In comparison, the formal two-electron-oxidation process of Sb during the formation of 5 from 2 leads to a significantly more positive δ for **5** (-6.0 mm s^{-1}) and a reduced eQV_{zz} (-9 mm s^{-1}) . These observations are in accordance with the isomer shift changes observed with the oxidation process of **VI** to **VII**. In fact, the 5s versus 5p orbital population calculated for the Sb atom of **5** is similar to that calculated for compound **VII** (Figure S27). Accordingly, the electronic situation of the Sb atom of complex **5** should resemble that of our Rh/Sb complex **VII**, i.e., which

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Table 3. NCs of the Sb and Pt Atoms as wel	ell as for Their Coordinated Ligands"
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	$1 \ Sb^4 \ Pt^4$	$2 \text{ Sb}^4 \text{ Pt}^4$	3^+ Sb ⁶ Pt ⁴	4 Sb ⁶ Pt ⁴	5 Sb ⁶ Pt ⁴	6 Sb ⁵ Pt ⁴
Sb	0.85	0.92	1.26	1.20	2.11	1.20
Pt	0.00	0.02	0.03 (Pt1), 0.03 (Pt2)	0.03 (Pt1), 0.06 (Pt2)	0.02	0.30
μ-pyS	-0.35, -0.35	-0.37, -0.36	-0.30, -0.28 (Pt1), -0.30, -0.29 (Pt2)	-0.35, -0.33 (Pt1), -0.32, -0.28 (Pt2)	-0.29, -0.29	-0.24, -0.24, -0.23, -0.22
PPh ₃	0.26	0.25	0.42, 0.42	0.37	0.35	
R	-0.41 (pyS)	-0.45 (Ph)		-0.38 (pyS)	-1.42 (C ₆ Cl ₄ O ₂), -0.48 (Ph)	-0.57 (Cl)
	Sb^{+II} - Pt^{+I}	Sb^{+II} - Pt^{+I}	$\begin{array}{c} Pt1^{+I}-Sb^{+II}\rightarrow Pt2^{+II},\\ Pt1^{+II}\leftarrow Sb^{+II}-Pt2^{+I}\end{array}$	$Pt1^{+I}-Sb^{+II}\rightarrow Pt2^{+II}$	Sb ^{+IV} -Pt ^{+I}	Sb ^{+III} ←Pt ^{+II}
a .						

^aThe CNs of Sb and Pt are given for each complex as superscripts.

shows a situation close to that of pentavalent Sb (with highly covalent Rh–Sb bond contributions) but with a tendency toward the trivalent state (significant contributions of the Sb \rightarrow Rh canonical form). The δ value of -14.5 mm s^{-1} of the signal of complex 6 (with a pronounced eQV_{zz} of 14.2 mm s⁻¹) represents the most negative value in the series of complexes studied herein and is even more negative than the signal of VI, i.e., in the range of trivalent Sb complexes. This is well in accordance with the calculated valence-shell orbital populations of its Sb atom (Figure S27).

NLMO Calculations. This method allows a look at the atomic contributions to the Pt–Sb bonds using NLMO calculations on the DFT level of theory (based on the atomic coordinates determined by X-ray structure analysis) as an indicator of the nature of this bond, i.e., Pt–Sb (X-type), Pt→Sb (Z-type), or Pt←Sb (L-type). Within this discussion, the anionic (pyS, Cl, and Ph) or neutral (PPh₃) ligands are formally separated from the di- or trinuclear core, thus giving the formal oxidation number (ON) of the metal core: (Pt/Sb)^{ON}. The data of the relevant NLMOs, which can be interpreted as Pt–Sb bonds or Sb- or Pt-located LPs, are summarized in Table 2, and selected NLMOs are depicted in Figure 6 (others are given in the Supporting Information).

For 1 and 2 [featuring $(Pt/Sb)^{+III}$ cores], we found LP NLMOs at Sb as well as localized NLMOs of the Pt-Sb bonds [degree of localization given as "% BD", i.e., percentage of parent natural bonding orbitals (NBOs)]. In both complexes, the Pt and Sb atoms contribute similarly to the Pt-Sb bond (in both cases, 49% Pt and 47% Sb). Hence, the Sb ligand atoms of 1 and 2 are of the X-type (covalent Pt-Sb bonds). The Sb atom provides basically 5p electron density toward these Pt-Sb bonds (1, 12% 5s, 88% 5p; 2, 14% 5s, 86% 5p), and the LP NLMOs of 1 and 2 at Sb exhibit mainly 5s orbital characteristics (1, 82% 5s, 18% 5p; 2, 76% 5s, 24% 5p). Figure 6 (left) displays the two relevant NLMOs of 1 [the LP(Sb) and BD(Pt-Sb) NLMOs of 2 are similar]. The formation of 1 and 2 from RSb(pyS)₂ (R = pyS, Ph) and $[Pt(PPh_3)_4]$ with retention of the LP at Sb may, at first glance, suggest the interpretation as $(Pt \rightarrow Sb)^{+III}$ complexes featuring dative bonds (Z-type Sb ligands). The occurrence of a covalent Pt-Sb bond (X-type), however, is clearly due to charge delocalization within the bridging pyS ligands. Because of the covalent Pt-Sb bonds, formal ONs of Pt^{+I}-Sb^{+II} have to be assigned to the (Pt/Sb)^{+III} cores. At this stage, we have to point out that ONs are based on formalisms, which can give misleading results, especially for bimetallic complexes. For instance, the formulation of even (Sb) or odd (Pt) ONs suggests paramagnetic species, which are clearly not present. This confusion just results from the formal homolytic splitting of the unpolar Pt-Sb bond (in a manner similar to that for Sb^{+II}

in Ph₂Sb-SbPh₂, which is diamagnetic and bears trivalent Sb atoms, but nonetheless, has the formal ON +II of its Sb atoms). The discussion of the natural charges (NCs) of the Pt and Sb atoms of 1-6 will shed more light on the differences between the real charges present at the metal atoms (vide infra). The cation 3^+ features a $(Pt/Sb/Pt)^{+V}$ core (four monoanionic pyS ligands with overall charge 1+) and is formed in a formal two-electron-oxidation process from 1 [the (Pt/Sb)^{+III} core; the Sb atom of the second equivalent of 1 forms the Sb^{+III} anion, vide supra]. Also, for 3^+ , NLMO analysis finds two localized and similar (symmetric molecule) Pt-Sb bonds. In this complex, both of them are formed by a larger fraction of Sb contribution (61%) and less Pt contribution (35%) (i.e., polarization of the bonds toward Sb), with almost equal contribution of the 5s (54%) and 5p (46%) electron densities of Sb. A percentage of the Sb contribution similar to that of the Pt-Sb bond can be found for Pt complexes with coordinated SbPh₃ (e.g., [PtCl₂(SbPh₃)₂];²⁸ see the Supporting Information) and thus for a ligand typically regarded as of the L-type. We found the bonding in 3^+ to be best described by intermediate L/X-type Sb ligands, i.e., the resonance structures featuring (Pt1^{+I} $b^{HI} \rightarrow Pt2^{HI})^{+V}/(Pt1^{HI} \leftarrow Sb^{HI} - Pt2^{H})^{+V}$, using the formalisms mentioned above. An interpretation as a $(Pt1^{+II} \leftarrow Sb^{+I} \rightarrow$ Pt2^{+II})^{+V} system would represent another alternative, but a comparison with compound 4 is in support of the former interpretation: Because of the asymmetric substitution pattern in 4 [also $(Pt/Sb/Pt)^{+V}$ core], the two Pt-Sb bonds are treated entirely different by NLMO analysis (Figure 6, second from the right): The Sb-Pt1 NLMO (PPh₃-substituted Pt) consists of 52% Sb and 37% Pt contributions, with Sb providing almost exclusively p density (7% 5s and 93% 5p), and an Sb-located LP with high 5s character (94% s and 6% p) donates into the antibonding Pt-S orbital (S trans to Sb, analyzed by the second-order perturbation theory). Hence, the unsymmetrical substitution pattern of the Pt atoms of 4 converts the sp hybrid orbitals of Sb (as found in 3^+) to distinct orbitals with pronounced 5s or 5p orbital characteristics, respectively, in their Sb-Pt interactions and formal ONs of $(Pt1^{+I}-Sb^{+II}\rightarrow Pt2^{+II})^{+V}$ can be derived. The $Sb(\mu-pyS)_2Pt$ - (PPh_3) motif in 4 resembles the electronic features of those in complexes 1 and 2, i.e., Sb-localized LP with notable 5s orbital characteristics and the Pt-Sb bond with similar contributions of Pt and Sb (p electron density contribution of Sb; Figure 6). It should be noted that there is a slight degree of delocalization of the orbital situation in 4 across the Pt-Sb-Pt core [BD(Pt1-Sb) 86%, 5% Pt2 contribution; LP(Sb) 78%, 9% Pt1, 6% s contribution]. However, the overall electronic situation can be explained by the bonding situations described above. NLMO analysis of 5, featuring a $(Pt/Sb)^{+V}$ core, finds

X-type Pt-Sb bonds with similar Sb (55%; 62% 5s and 38% 5p) and Pt (41%; 34% 6s and 65% 5d) contributions. Because of the formal two-electron-oxidation process at Sb, no LP(Sb) is present in 5 and a Pt+I-Sb+IV resonance structure can be derived. In contrast to 1 and 2, for both compounds 4 and 5, a slight polarization of the Pt-Sb bond toward Sb is predicted by NLMO. Therefore, these bonds may also be considered to be intermediate between Pt-Sb and Pt←Sb. In complex 6 (Figure 6, right), a LP with high 5s character (85% 5s and 15% 5p) is located at Sb. In comparison to complexes 1-5, another entirely different Pt–Sb interaction within the (Pt/Sb)^{+V} core is observed for this complex: The bond is strongly polarized toward Pt, and NLMO treats this bond as LP(Pt) with 73% Pt (2% 6s and 98% 5d) and 22% Sb (14% 5s and 86% 5p) contributions. Second-order perturbation theory reveals LP- $(Pt) \rightarrow Sb$ interaction of this LP with an Sb(p) orbital. Hence, the Sb atom of 6 clearly exhibits Z-type ligand characteristics, and the bond can be described using a $Pt^{+II} \rightarrow Sb^{+III}$ resonance structure. Because of the problems associated with the assignment of formal ONs, we gained further insight into the charge distribution of the metal atoms and surrounding ligands of complexes 1-6 by analyzing the NCs (Table 3).

For 1 and 2, the sum of the NCs of Sb and Pt is significantly smaller than the formal ON of +III of the Pt/Sb core, which is due to charge compensation by the surrounding ligands; certainly, no isolated Sb and Pt cations are present. This charge compensation, which is more pronounced for softer ligands, thus leads to a smaller NC of Sb in 1 (Sb-S bond) compared to that in 2 (Sb–C bond). Resulting therefrom, the overall NC of the κ S-bound pyS ligand in 1 is less negative (-0.41 e) than that of the Ph substituent of 2 (-0.45 e). The overall more positive NCs for Sb compared to Pt in 1 and 2 are in agreement with the Sb^{+II}-Pt^{+I} formulation. In complex 3⁺, all fragments are more positively charged than those in 1 and 2, which is due to the overall charge of 1+ of the complex. The most striking differences are found with the Sb atom (1.26 e)and PPh₃ ligands (0.42 e). One may suggest the formal twoelectron oxidation of 1 into 3^+ to affect the Sb atom to a large extent; however, this enhanced positive charge is mainly a result of (i) the presence of four rather hard and electronegative atoms (N atoms, less charge compensation) in the coordination sphere of Sb in 3^+ and (ii) the incorporation of the LP Sb 5s electron density (as found in 1 and 2) into Sb-Pt bonds.²⁹ A formal two-electron-oxidation process at Sb during the conversion of 2 into 5 is accompanied by a much more pronounced increase of the NC of Sb (vide infra). The NCs of Pt of 1 and 3⁺ are almost identical; however, the PPh₃ ligands of 3^+ (0.42 e) reveal a distinctly more positive charge than those of 1 (0.26 e), and the NC of the pyS ligands is less negative; i.e., the enhanced positive charge of Pt is completely compensated for by the ligands. This "enhanced but compensated" positive charge of Pt as well as polarization of the Pt-Sb bonds toward Sb is supportive of the Pt^{+I} -Sb^{+II} \rightarrow Pt^{+II} resonance structures for 3⁺. Because of the absence of an overall positive charge, the NCs of different structural moieties of the unsymmetrically substituted complex 4 are slightly more negative than those in 3^+ . The NCs of the Pt atoms, however, are similar to those of 3^+ . Moreover, there is a trend toward the Pt1 atom and its surrounding two pyS ligands, being more negatively charged (Pt1, 0.03; pyS, -0.35, -0.33; sum, -0.65 e) than Pt2 and its pyS ligands (Pt2, 0.06; pyS, -0.32, -0.28; sum, -0.52 e). This can be expressed by the resonance structure (Pt1^{+I}-Sb^{+II} \rightarrow Pt2^{+II}) for 4. Unfortunately, we could

not record a ¹²¹Sb Mössbauer spectrum of **4** (vide supra). The unsymmetrical charge distribution of the Sb atom of 4 could result in a more pronounced eQV_{zz} in this complex; however, δ is expected to be essentially equal to that of 3⁺ (similar NCs of Sb in 3^+ and 4 with the same coordination geometry of Sb) and, therefore, 4 can be regarded as a trivalent Sb species. In complex 5, the most obvious feature is the enhanced NC of Sb (2.11 e), similar to that of VII (2.27 e) or a series of Ru/Sb complexes (2.03-2.35 e).³⁰ In terms of the canonical forms, the bonding in 5 can be best described with both Pt+I-Sb+IV and Pt^{+II}←Sb^{+III} canonical forms (see the detailed discussion in ref15, also with respect to the quantum-chemical calculations of the Sb^{+III} and Sb^{+V} reference compounds). In 6, the Pt atom is more positive (0.30 e) than those in 1-4, which are already damped by the pyS ligands' charge compensation (charge of pyS^- in 6: av. -0.23 e, least negative value found in the series). The NC of Sb (1.20 e) is close to those found for 3 and 4. Hence, a $Pt^{+II} \rightarrow Sb^{+III}$ situation is best to be formulated for this paddle-wheel-shaped compound.

CONCLUSIONS

We have accessed a variety of Pt/Sb complexes featuring the bridging pyS ligand and analyzed them by means of X-ray diffraction analyses, multinuclear NMR spectroscopy, ¹²¹Sb Mössbauer spectroscopy, and NLMO calculations. Special emphasis was given on the Pt-Sb bonding situations, which were shown to be very different in nature. The most important result is the observation of L-, X-, and Z-type coordination modes, all realized by trivalent (i.e., LP-bearing) Sb ligands. The binuclear complexes 1 and 2 feature X-type Sb ligands. The stoichiometric oxidation of 1 using *o*-chloranil gives the trinuclear, cationic, and symmetrically substituted complex 3⁺, and it was shown that both the Sb and Pt atoms (or the Pt/ PPh₃ motifs) are affected by the oxidation process. PPh₃ ligand exchange at 3^+ for pyS gives the unsymmetrically substituted compound 4. Compounds 3^+ (with its polarization of the metal-metal bond toward Sb) and 4 (with two different Pt-Sb bonds, including L-type Sb) represent entirely new motifs of pnictogen coordination chemistry as well as unexpected Ltype coordination modes of Sb. The oxidation of 2 by ochloranil furnishes 5 with Sb in an intermediate X/L-type situation. This reaction serves as a reference for the twoelectron oxidation of Sb, compared to the oxidation of 1 leading to 3⁺, which affects the Pt atoms of the heterometallic core and their ligands to a large extent. The Z-type coordination mode of trivalent Sb was realized in compound 6. This $Pt^{+II} \rightarrow Sb^{+III}$ complex represents a rare example of a trivalent Sb compound serving as an electron-pair acceptor toward a TM. At this stage, we have to point out that formal ONs of the metal atoms of complexes 1-6 should not be overinterpreted because their assignment relies on the formalism based on certain Lewis structures. For instance, the unpolar Pt-Sb bonds in 1 and 2 (X-type) give rise to the formulation of ONs Sb^{+II}-Pt^{+I}. A similar bonding situation (LP at Sb and a rather unpolar Sb-Pt bond) is present in 4 and, therefore, also Sb^{+II}-Pt^{+I} has to be considered. However, this does not account for the larger NC of Sb, which would better be described by ONs of Sb+III-Pt⁰. NCs, however, are strongly influenced by different charge compensations from hard versus soft donor atoms in the metal atoms' coordination spheres. Hence, in those complexes, it is recommended to differentiate between trivalent (LP-bearing) and pentavalent Sb species. In this regard, the stand-out data for complexes 1**6** are the ¹²¹Sb Mössbauer spectroscopic parameters, which agree well with the results of the NLMO calculations (localization of Sb-located LPs or Sb–Pt bonds of pronounced Sb character with predominant Sb 5s orbital contributions).

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out under an atmosphere of dry argon using standard Schlenk techniques. Solvents were dried as follows: distillation over sodium (Na)/benzophenone [THF and diethyl ether (Et₂O)], distillation over Na (mesitylene, pentane, hexane, and toluene), and storage over molecular sieves 3 Å (dichloromethane, DCM). Furthermore, all solvents were routinely degassed using three freeze-pump-thaw cycles, although the use of dry and oxygen-free solvents is not necessary for all reactions. $[PtCl_2(PPh_3)_2]$,³¹ Sb(pyS)₃,¹⁶ PhSb(pyS)₂,¹⁷ [PtCl(pyS)(PPh_3)],¹⁷ and PhICl₂³² were synthesized according to literature protocols. All other chemicals were commercially available and were used as received. NMR spectroscopy. NMR spectra were measured on an ASCEND400 or AVANCE500 spectrometer (Bruker) at room temperature. The spectra are internally referenced to residual solvent signals (¹H and ¹³C; see ref33 for chemical shifts of those signals relative to tetramethylsilane) or external 85% H₃PO₄ (³¹P). Chemical shifts δ are given in parts per million. ¹H and ¹³C NMR signals have been assigned to the respective atoms using two-dimensional NMR techniques (HSQC, HMBC, and NOESY). The signals of the protons of the pyridine-2-thiolate (pyS⁻) ligand reveal couplings to all other protons of the parent pyS ligand, which, in most cases, could be resolved. Hence, each signal is split into three independent doublets (annotation as "d of dd" and multiplet m if coupling could not be resolved). Labeling of the atomic positions of the pyS ligand: N¹- $C^{2} = S - (C^{3} - H^{3}) - (C^{4} - H^{4}) - (C^{5} - H^{5}) - (C^{6} - H^{6})$. The different positions (coordination modes) of the pyS ligand are given as μ (bridging) and κ S (S-bound). The ³¹P{¹H} CP MAS NMR spectrum of 4 was measured using an AVANCE III HD 400 WB spectrometer (Bruker). The sample was placed in a 2.5 mm ZrO₂ rotor and rotated at 15 kHz. The spectrum was referenced against external (NH₄)- H_2PO_4 (1.1 ppm relative to 85% H_3PO_4). Elemental analyses. The C/H/N/S analyzer Vario Micro Cube (Elementar) was used for elemental analyses. ¹²¹Sb Mössbauer spectra were recorded at 5 K using a Ba^{121m}SnO₃ source. Samples were enclosed in poly(methyl methacrylate) containers. The WinNormos for Igor program package was used for data fitting.³⁴ Computational details. All calculations were carried out with Gaussian09.35 H-atom optimization of the atomic coordinates obtained from the X-ray diffraction analyses was performed with DFT-PBEPBE def2-TZVPP. The NBO/NLMO analyses were performed using NBO6.0.36 The DFT-B3LYP 6-311+G(d) (C, H, N, O, S, Cl, and P) and SDD (Sb and Pt) basis sets were applied, including the second-order Douglas-Kroll-Hess scalar relativistic approach. X-ray crystallography. For determination of the X-ray structure, a crystal of the appropriate size was attached to a glass capillary with a thin-film of silicone grease. Data sets were collected on an IPDS-2T diffractometer (STOE) using Mo K α radiation (0.71073 Å). Structures were solved with direct methods (ShelXS)³ and refined in full-matrix least-squares cycles against F^2 (ShelXL).³⁸ H atoms were refined isotropically, placed in geometrically idealized positions, and constrained to ride on their pivot atoms with $U_{iso}(H) =$ $1.2U_{iso}(C)$. The solvent-accessible voids of the structures of 1.2THF, 3^{III}·0.5DCM, 3^V·DCM, 4·3THF, and 6 (void contains practically no solvent of crystallization) were analyzed with Squeeze, as implemented in PLATON.³⁹ The parameters of data collection and structure refinement can be found in the Supporting Information. CIF files for CCDC 1543916 (1·2THF), 1996585 (2), 1996586 (3^{III}·0.5DCM), 1996587 (3^V·DCM), 1996379 (4·3THF), 1996588 (4[#]·THF), 1996380 (5), 1996381 (6.1.5DCM), 1996382 (6) have been deposited with the Cambridge Crystallographic Data Center.

[Pt(PPh₃)₄]. This compound can be prepared according to literature protocols from K_2PtCl_4 , PPh₃, and KOH.⁴⁰ However, this procedure furnishes a fine powder of the product. Recrystallization of [Pt(PPh₃)₄] can afford the 3-fold-substituted derivative [Pt(PPh₃)₃].

We were aiming at the synthesis of a coarse crystalline material of high purity. Hence, we have developed a procedure starting from $[PtCl_2(PPh_3)_2]/PPh_3$ and N_2H_4 as the reducing agent. According to the preparation of the analogous palladium compound,⁴¹ the reaction was performed in a high boiling solvent and the product crystallized upon cooling. Surprisingly, to the best of our knowledge, this protocol has not appeared in the literature. The product was obtained as a coarse crystalline material in a one-pot reaction in mesitylene without the need of recrystallization. The reaction in dimethyl sulfoxide (which was reported for the preparation of $[Pd(PPh_3)_4]$), however, was found to give an orange-red product, probably because of side/ decomposition reactions. The results of elemental analysis agree well with the calculated values for $[Pt(PPh_3)_4]$, and the melting point is in accordance with the literature. [PtCl₂(PPh₃)₂] (1.80 g, 2.28 mmol) and PPh₂ (1.50 g, 5.72 mmol) were suspended in mesitylene (70 mL) and heated up to about 150 °C using an oil bath. The white suspension was then cooled to about 100 °C, and N2H4·H2O (1.0 mL, 20.6 mmol) was added dropwise, whereupon an orange solution formed. This solution was allowed to slowly cool to room temperature overnight without stirring. After 2 days, the yellow crystals that had formed during this time were filtered off, washed with mesitylene (2 \times 5 mL), ethanol $(2 \times 5$ mL), thoroughly with water $(3 \times 10$ mL), and finally with ethanol $(3 \times 10 \text{ mL})$, and dried under vacuum. Yield: 2.30 g (1.85 mmol, 81%). Anal. Calcd for $C_{72}H_{60}P_4Pt$ ($M_r = 1244.22$ g mol⁻¹): C, 69.50; H, 4.86. Found: C, 69.26; H, 4.77. Mp: 125-129 °C (dec).

 $[(\kappa S-pyS)Sb(\mu-pyS)_2Pt(PPh_3)]$ (1). $Sb(pyS)_3$ (150 mg, 332 μ mol) and $[Pt(PPh_3)_4]$ (420 mg, 338 μ mol) were stirred in THF (5 mL) at room temperature, causing the formation of a clear yellow solution. Upon further stirring at room temperature, a yellow solid precipitated and the suspension was warmed slightly using a water bath, resulting in a clear solution. This solution was then kept at -21 °C, and after 2 days, yellow crystals of 1.2THF (suitable for X-ray diffraction analysis) had formed, which were isolated by decantation and washed with Et₂O (2 \times 3 mL). Upon drying, the product loses its solvent of crystallization, as proven by NMR spectroscopy and elemental analysis (color change from yellow toward orange upon drying). Yield: 270 mg (297 μ mol, 89%) of an orange crystalline material. ¹H NMR (500.13 MHz, CD₂Cl₂): δ 6.64 (d of dd, ${}^{3}J_{H-H} = 7.0/5.6$ Hz, ${}^{4}J_{H-H} = 1.2$ Hz, 2H, H-5 μ -pyS), 7.01 (d of dd, ${}^{3}J_{H-H} = 7.3/4.9$ Hz, ${}^{4}J_{H-H} = 1.1$ Hz, 1H, H-5 κ S-pyS), 7.15 (d of dd, ${}^{3}J_{H-H} = 8.3/7.0$ Hz, ${}^{4}J_{H-H} = 1.7$ Hz, 2H, H-4 μ -pyS), 7.23 (m, ${}^{3}J_{H-H} = 8.3$ Hz, 2H, H-3 μ pyS), 7.30 (m, ${}^{3}J_{H-H} = 8.0$ Hz, 1H, H-3 κ S-pyS), 7.41 (d of dd, ${}^{3}J_{H-H}$ = 8.0/7.3 Hz, ${}^{4}J_{H-H}$ = 1.9 Hz, 1H, H-4 κ S-pyS), 7.45–7.48 (mm, 9H, $Ph_{meta/para}$), 7.71 (m, 6H, Ph_{ortho}), 8.29 (m, ${}^{3}J_{H-H}$ = 5.6 Hz, 2H, H-6 μ -pyS), 8.55 (d of dd, ${}^{3}J_{H-H} = 4.9$ Hz, ${}^{4}J_{H-H} = 1.9$ Hz, ${}^{5}J_{H-H} = 0.9$ Hz, 1H, H-6 κ S-pyS). ¹³C{¹H} NMR (125.75 MHz, CD₂Cl₂): δ 117.3 (C-5 μ-pyS), 119.6 (C-5 κS-pyS), 125.3 (C-3 κS-pyS), 126.5 (satellites: ${}^{3}J_{Pt-C} = 64 \text{ Hz}, C-3 \mu\text{-pyS}), 128.4 (d, {}^{3}J_{P-C} = 10 \text{ Hz}, Ph_{meta}), 130.4 (d,)$ ${}^{1}J_{P-C} = 45 \text{ Hz}, \text{ Ph}_{\text{ipso}}$), 130.9 (d, ${}^{4}J_{P-C} = 2 \text{ Hz}, \text{ Ph}_{\text{para}}$), 135.5 (d, ${}^{2}J_{P-C}$ = 11 Hz, Ph_{ortho}), 135.9 (C-4 μ-pyS), 136.3 (C-4 κS-pyS), 146.8 (satellites: ${}^{3}J_{Pt-C} = 25$ Hz, C-6 μ -pyS), 149.7 (C-6 κ S-pyS), 161.8 (d, ${}^{4}J_{P-C} = 5$ Hz, C-2 κ S-pyS), 166.9 (d, ${}^{3}J_{P-C} = 18$ Hz, C-2 μ -pyS). ³¹P{¹H} NMR (202.45 MHz, CD₂Cl₂): δ 34.7 (satellites: ¹J_{Pt-P} = 2226 Hz). Anal. Calcd for $C_{33}H_{27}N_3S_3PPtSb$ ($M_r = 909.60 \text{ g mol}^{-1}$): C, 43.57; H, 2.99; N, 4.62. Found: C, 43.96; H, 3.04; N, 4.43. Mp: 246-149 °C.

[PhSb(μ-pyS)₂Pt(PPh₃)] (2). PhSb(pyS)₂ (70 mg, 167 μmol) and [Pt(PPh₃)₄] (218 mg, 177 μmol) were stirred in Et₂O (5 mL) at room temperature for 12 h. The yellow product that had formed during this time was then filtered off, washed with Et₂O (3 × 2 mL), and dried under vacuum, yielding 127 mg (145 μmol, 87%) of a yellow powder. ¹H NMR (500.13 MHz, CD₂Cl₂): δ 6.70 (m, 2H, H-5 pyS), 7.12 (m, 3H, SbPh_{para}/H-4 pyS), 7.18 (m, 2H, SbPh_{meta}), 7.23 (m, ³J_{H-H} = 8.3 Hz, 2H, H-3 pyS), 7.48 (m, 9H, PPh_{meta/para}), 7.76 (m, 6H, PPh_{ortho}), 8.18 (m, ³J_{H-H} = 7.1 Hz, 2H, SbPh_{ortho}), 8.25 (m, ³J_{H-H} = 5.4 Hz, 2H, H-6 pyS). ¹³C{¹H} NMR (125.75 MHz, CD₂Cl₂): δ 117.3 (C-5 pyS), 126.7 (satellites: ³J_{P+C} = 66 Hz, C-3 pyS), 127.4 (SbPh_{para}), 128.3 (d, ³J_{P-C} = 11 Hz, PPh_{meta}), 128.5

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(SbPh_{meta}), 130.7 (d, ¹ J_{P-C} = 44 Hz, PPh_{ipso}), 130.8 (d, ⁴ J_{P-C} = 2 Hz, PPh_{para}), 135.2 (C-4 pyS), 135.4 (d, ² J_{P-C} = 11 Hz, PPh_{ortho}), 139.0 (satellites: ³ J_{P+C} = 33 Hz, SbPh_{ortho}), 146.4 (satellites: ³ J_{P+C} = 28 Hz, C-6 pyS), 149.3 (d, ³ J_{P-C} = 4 Hz, SbPh_{ipso}), 167.2 (d, ³ J_{P-C} = 18 Hz, C-2 pyS). ³¹P{¹H} NMR (202.45 MHz, CD₂Cl₂): δ 32.7 (satellites: ¹ J_{Pt-P} = 2201 Hz). Anal. Calcd for C₃₄H₂₈N₂PPtS₂Sb (M_r = 876.54 g mol⁻¹): C, 46.59; H, 3.22; N, 3.20. Found: C, 46.64; H, 3.13; N, 3.03. Mp: 190–200 °C. The product that was obtained by this method contains an impurity of unknown identity (less than 2%), as indicated by ¹H (pyS signals among others) and ³¹P{¹H} (28.6 ppm in CD₂Cl₂), no OPPh₃) NMR spectroscopy. For the reaction of 2 with *o*-chloranil to afford 5, the material was used as such as the impurity could not completely be removed by recrystallization. Single crystals were grown via gas-phase diffusion of Et₂O into a THF solution over a period of 3 days.

 $[(PPh_3)Pt(\mu-pyS)_2Sb(\mu-pyS)_2Pt(PPh_3)]^+[Sb(C_6Cl_4O_2)_3]^- (3^{V}).$ Complex 1 (157 mg, 173 µmol) and o-chloranil (70 mg, 285 μ mol) were stirred in toluene (5 mL) at room temperature. After 3 h, the yellow product was filtered off, washed with toluene $(2 \times 0.5 \text{ mL})$ and pentane (2 \times 0.5 mL), and dried under vacuum. Yield: 125 mg (54 μ mol, 62%) of a yellow powder. ¹H NMR (500.13 MHz, CD_2Cl_2): δ 6.77 (m, ${}^{3}J_{H-H}$ = 5.7 Hz, ${}^{4}J_{H-H}$ = 1.2 Hz, 4H, H-5 pyS), 7.31 (m, ${}^{3}J_{H-H} = 8.3/7.0$ Hz, ${}^{4}J_{H-H} = 1.6$ Hz, 4H, H-4 pyS), 7.46 (m, ${}^{3}J_{H-H}$ = 8.3 Hz, 4H, H-3 pyS), 7.51 (m, 12H, Ph_{meta}), 7.57 (m, 6H, Ph_{para}), 7.68 (m, 12H, Ph_{ortho}), 9.27 (m, ${}^{3}J_{H-H} = 5.5$ Hz, 4H, H-6 pyS). ${}^{13}C{}^{1}H{}$ NMR (125.75 MHz, CD₂Cl₂): δ 118.1 (C-Cl C₆Cl₄O₂), 118.2 (C-5 pyS), 122.7 (C-Cl C₆Cl₄O₂), 126.4 (C-3 C₆Cl₄O₂), 118.2 (C-5 pyS), 122.7 (C-Cl C₆Cl₄O₂), 123.1 (C-5 pyS), 128.0 (d, ${}^{1}J_{P-C} = 57$ Hz, Ph_{ipso}), 128.9 (m, ${}^{3}J_{P-C} = 11$ Hz, Ph_{meta}), 132.1 (Ph_{para}), 135.1 (m, ${}^{2}J_{P-C} = 11$ Hz, Ph_{ortho}), 138.5 (C-4 pyS), 143.9 (C-O C₆Cl₄O₂), 148.1 (C-6 pyS), 160.9 (m, C-2 pyS). ${}^{31}P{}^{1}H$ NMR (161.97 MHz, CD₂Cl₂): δ 28.4 (m, ${}^{1}J_{P+P} = 3310$) 3088 Hz, ${}^{3}J_{Pt-P} = 221$ Hz, ${}^{4}J_{P-P} = 47$ Hz). Anal. Calcd for $C_{74}H_{46}Cl_{12}N_4O_6P_2Pt_2S_4Sb_2$ ($M_r = 2336.50 \text{ g mol}^{-1}$): C, 38.04; H, 1.98; N, 2.40. Found: C, 37.72; H, 2.07; N, 2.32. Mp: 264-268 °C. Single crystals of 3^{V} ·DCM were grown by the slow evaporation of a DCM/hexane solution (2:1) exposed to air.

 $[(PPh_3)Pt(\mu-pyS)_2Sb(\mu-pyS)_2Pt(PPh_3)]^+[Sb(C_6Cl_4O_2)_2]^-$ (3^{III}). Complex 1 (70 mg, 77 µmol) and o-chloranil (19 mg, 77 µmol) were stirred in DCM (2.5 mL) at ambient temperature for 1 h, whereupon an orange solution formed. Afterward, hexane (2.5 mL) was added, and the volume of the solution was reduced under vacuum to about 3 mL, causing the precipitation of a yellow solid. This solid was filtered off, washed with hexane $(2 \times 0.5 \text{ mL})$, and dried under vacuum. The crude product was redissolved in DCM (1.5 mL), and the solution was layered with hexane (3 mL). After 3 days, the crystals of 3^{III} 0.5DCM (suitable for X-ray crystallography) were isolated by decantation, washed with hexane (2 \times 0.5 mL), and briefly dried under vacuum. Yield: 35 mg (16 μ mol, 43%). ¹³C{¹H} NMR (CD₂Cl₂, 100.62 MHz): δ 117.5 (C-Cl C₆Cl₄O₂), 118.2 (C-5 pyS), 119.4 (C-Cl C₆Cl₄O₂), 126.4 (C-3 pyS), 128.0 (d, ${}^{1}J_{P-C} = 57$ Hz, Ph_{ipso}), 128.9 (m, ${}^{3}J_{P-C} = 11$ Hz, Ph_{meta}), 132.1 (Ph_{para}), 135.1 (m, ${}^{2}J_{P-C} = 11 \text{ Hz}, \text{Ph}_{\text{ortho}}$), 138.5 (C-4 pyS), 148.1 (C-6 pyS), 150.5 (C-O C₆Cl₄O₂), 160.9 (m, C-2 pyS). Anal. Calcd for $C_{68}H_{46}Cl_8N_4O_4P_2Pt_2S_4Sb_2\cdot 0.5CH_2Cl_2$ ($M_r = 2133.09 \text{ g mol}^{-1}$): C, 38.57; H, 2.22; N, 2.63. Found: C, 37.92; H, 2.10; N, 2.60. ¹H and ³¹P{¹H} NMR spectra are analogous to those of 3^V.

[(PPh₃)Pt(μ -pyS)₂Sb(μ -pyS)₂Pt(κ S-pyS)] (4). Complex 3^V (90 mg, 38.5 μ mol) and LipyS (freshly prepared from pySH and *n*-BuLi in Et₂O, 7 mg would correspond to 60 μ mol of pure LipyS; see the Supporting Information) were layered with THF (1.5 mL) and stored at ambient temperature. After 3 days, the mother liquor was decanted off the orange crystals (4·3THF suitable for X-ray analysis), and the product was washed with THF (2 × 0.5 mL) and dried under vacuum, whereupon the crystals lost most of their THF content. Yield: 11 mg (8.1 μ mol, 21%) of 4·0.5THF. ³¹P{¹H} CP MAS NMR (162.04 MHz, $\nu_{rot} = 15$ kHz): δ 28.8 (¹ $J_{Pt-P} = 2991$ Hz). Anal. Calcd for C₄₃H₃₅N₅PPt₂S₅Sb-0.5C₄H₈O ($M_r = 1361.04$ g mol⁻¹): C, 39.71; H, 2.89; N, 5.15. Found: C, 39.74; H, 3.04; N, 4.81. The compound is practically insoluble in common organic solvents.

 $[(\kappa - O_1O_1 - C_6Cl_4O_2)PhSb(\mu - pyS)_2Pt(PPh_3)]$ (5). Complex 2 (150) mg, 171 μ mol) was suspended in THF (2.5 mL) at room temperature with continuous stirring. A solution of o-chloranil (42 mg, 171 μ mol) in THF (1 mL) was then slowly added to this suspension over a period of 1 h in order to avoid any local excess of the oxidizing agent. The orange solution resulting therefrom was exposed to gas-phase diffusion of Et₂O, whereupon brown crystals formed over a period of 5 days. Afterward, the product was isolated by decantation, washed with Et₂O (2×2 mL), and dried under vacuum. Yield: 80 mg (71 μ mol, 42%) of a brown crystalline compound. ¹H NMR (500.13 MHz, CD₂Cl₂): δ 6.79 (m, 2H, H-5 pyS), 7.25-7.34 (m, 5H, SbPh_{meta/para}/H-4 pyS), 7.52-7.58 (m, 11H, PPh_{meta/para}/H-3 pyS), 7.77 (m, 6H, PPh_{ortho}), 8.16 (m, ${}^{3}J_{H-H} = 7.1$ Hz, 2H, SbPh_{ortho}), 8.38 (m, ${}^{3}J_{H-H} = 5.9$ Hz, 2H, H-6 pyS). ${}^{13}C{}^{1}H{}$ NMR (125.75 MHz, CD_2Cl_2): δ 116.5 (C-Cl C₆Cl₄O₂), 118.9 (C-5 pyS), 127.5 (satellites: ${}^{3}J_{Pt-C} = 41$ Hz, C-3 pyS), 128.8 (d, ${}^{3}J_{P-C} = 11$ Hz, PPh_{meta}), 128.9 (d, ${}^{1}J_{P-C} = 53$ Hz, Ph_{ipso}), 129.2 (SbPh_{meta}), 130.1 (SbPh_{para}), 131.8 (d, ${}^{4}J_{P-C} = 2$ Hz, PPh_{para}), 133.0 (SbPh_{ortho}), 135.3 (d, ${}^{2}J_{P-C} = 11$ Hz, PPh_{ortho}), 139.0 (C-4 pyS), 144.8 (C-6 pyS), 158.3 (d, ${}^{4}J_{P-C} = 10$ Hz, C-O C₆Cl₄O₂), 160.4 (d, ${}^{3}J_{P-C} = 30$ Hz, C-2 pyS). C-Cl C₆Cl₄O₂ (probably very broad) and SbPh_{ipso} (low intensity of quaternary C in conjunction with Pt and P coupling) not observed. ${}^{31}P{}^{1}H$ NMR (202.45 MHz, CD_2Cl_2): δ 21.6 (satellites: ${}^{3}J_{Pt-P} = 3067$ Hz). X-rayquality crystals were obtained by recrystallization from a DCM/ hexane mixture (2:1) upon slow evaporation (exposed to air).

[Sb(µ-pyS)₄PtCl] (6). Method a. Compound 1 (100 mg, 110 μ mol) and PhICl₂ (45 mg, 164 μ mol) were stirred in DCM (0.5 mL) for 2 min. Afterward, the yellow solution was kept at room temperature without stirring, whereupon yellow crystals of 6· 1.5DCM (suitable for X-ray analysis) formed. The product was isolated after 3 days by decanting off the mother liquor, washed with DCM (2×0.5 mL), and finally dried under vacuum, whereupon the crystals lost DCM. Yield: 25 mg (28.5 µmol, 26%). Method b. In a Schlenk tube, the compounds $[PtCl(pyS)(PPh_3)]$ (82 mg, 140 μ mol) and Sb(pyS)₃ (63 mg, 139 μ mol) were layered with DCM (1 mL) and stored at room temperature. After 3 days, the mother liquor was decanted off the yellow crystals that had formed, and this product was washed with DCM $(2 \times 0.5 \text{ mL})$ and thoroughly dried under vacuum, yielding 14 mg (17.7 μ mol, 13%) of yellow crystals. ¹H NMR (500.13 MHz, CD_2Cl_2): δ 6.88 (m, ${}^{3}J_{H-H} = 5.7$ Hz, ${}^{4}J_{H-H} = 1.1$ Hz, 4H, H-5 pyS), 7.31 (d of dd, ${}^{3}J_{H-H} = 8.3/7.1$ Hz, ${}^{4}J_{H-H} = 1.7$ Hz, 4H, H-4 pyS), 7.51 (m, ${}^{3}J_{H-H} = 8.3$ Hz, ${}^{4}J_{H-H} = 1.1$ Hz, 4H, H-3 pyS), 8.04 (d of dd, ${}^{3}J_{H-H} = 5.7$ Hz, ${}^{4}J_{H-H} = 1.7$ Hz, ${}^{5}J_{H-H} = 1.0$ Hz, 4H, H-6 pyS). Anal. Calcd for $C_{20}H_{16}ClN_4S_4PtSb$ ($M_r = 792.92 \text{ g mol}^{-1}$): C, 30.29; H, 2.03; N, 7.07. Found: C, 29.92; H, 2.06; N. 6.71. Mp: 290 °C (dec). The solubility of this complex in organic solvents is not sufficient to record ¹³C{¹H} NMR spectra. Using THF in method b as a solvent, another modification devoid of a solvent of crystallization (which, however, features solvent-accessible voids of 217 Å³) can be obtained.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02615.

Depiction of NMR spectra of all complexes, synthetic procedures for LipyS and $4^{\#}$, depiction of molecular structures of 3^+ in 3^{III} , antimony catecholate anions, and $4^{\#}$, parameters of data collection and structure refinement, detailed discussion of the ${}^{31}P{}^{1}H{}$ NMR spectrum of 3^+ , and additions to the NLMO calculations (graphics of selected NLMOs, calculated 5s vs 5p orbital electronic populations of compounds 1, 2, 3^+ , and 4-6) (PDF)

Accession Codes

CCDC 1543916, 1996379–1996382, and 1996585–1996588 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.

AUTHOR INFORMATION

Corresponding Author

Jörg Wagler – Institut für Anorganische Chemie, Technische Universität (TU) Bergakademie Freiberg, 09599 Freiberg, Germany; orcid.org/0000-0001-5968-2331; Email: joerg.wagler@chemie.tu-freiberg.de

Authors

Erik Wächtler – Institut für Anorganische Chemie, Technische Universität (TU) Bergakademie Freiberg, 09599 Freiberg, Germany

Robert Gericke – Institut für Anorganische Chemie, Technische Universität (TU) Bergakademie Freiberg, 09599 Freiberg, Germany

Theresa Block – Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster, 48149 Münster, Germany

Rainer Pöttgen – Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster, 48149 Münster, Germany

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.0c02615

Notes

The authors declare no competing financial interest.

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