[Pd₄(μ₃-SbMe₃)₄(SbMe₃)₄]: A Pd(0) Tetrahedron with μ₃-Bridging Trimethylantimony Ligands

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Supporting Information

ABSTRACT: The palladium(II) chlorostibine complex [PdCl₂(SbMe₃)₂]₂ has a dimeric structure in the solid state, stabilized by hyper-coordination at the Lewis amphoteric Sb centers. Reaction with 8 equiv of MeLi forms [Pd₄(μ₃-SbMe₃)₄(SbMe₃)₄], whose structure comprises a tetrahedral Pd(0) core with four terminal SbMe₃ ligands and four μ₁-SbMe₃ ligands, one capping each triangular Pd₃ face. Density functional theory calculations, supported by energy decomposition analysis and the natural orbitals for chemical valence scheme, highlight significant donor and acceptor orbital contributions to the bonding between both the terminal and the bridging SbMe₃ ligands and the Pd₄ core.

Despite their ubiquity in modern coordination chemistry, it was long thought that phosphine ligands and their heavier pnictine congeners (PnR₃; Pn = P, As, Sb, Bi) were terminal donors only, while other π-acceptor ligands such as CO are found to be more frequent than one metal center. Werner was the first to challenge this concept, with the isolation of a Rh₂ dimer bridged by SbMe₃ (Figure 1, i), its subsequent ligand metathesis giving rise to the first examples of μ₁-bridging PR₃ and AsR₃.¹,² Despite this breakthrough, very few other systems with bridging pnictines have since been characterized; Balch isolated a few examples of PF₃ triply bridging a Pd₃ triangle (Figure 1, ii),³,⁴ and Gabbaï recently reported the complexation of a tetradentate P₅N₅ ligand (P₅ = Sb, Bi) with a M₂ triangle (M = Cu, Ag) in which the heavy pnictine donor is supported centrally above the M₂ face (Figure 1, iii).³ Because of the rarity of such species, little is known about the nature of the bonding in these complexes. Based on the limited examples, the bridging mode seems to feature a significant component of acceptance by the ligand and is best stabilized by late transition metals in low oxidation states and strongly π-accepting or heavier, more Lewis acidic pnictines.³

There has been a surge of recent interest in the “non-innocent” behavior of coordinated heavy pnictines, which in several cases demonstrate redox reactivity or anion exchange at Pn in preference to the transition metal center.⁶,⁷ They are also prone to hyper-coordination, forming intra- or intermolecular secondary acceptor interactions with electronegative donor atoms; this behavior is enhanced by electronegative substituents on the pnictine, which increase the Lewis acidity of the Pn center.⁸ We have previously demonstrated that increasing the number of halide substituents in SbBr₃Me₃⁻ (n = 0–2) increases the π-acceptor capacity of the stibine ligand.⁹ While triorganopnictines are σ-donor/π-acceptor ligands, halide-substituted Sb and Bi centers have been seen to act as σ-acceptors toward electron-rich transition metals, giving rise to complexes with highly unusual electronic structures.¹⁰⁻¹⁴

We report here an unusual dimeric Pd(II) complex of SbMe₃Cl which demonstrates significant Lewis acidity of the bound holostibine. The reaction of MeLi leads to formation of an unexpected Pd(0) cluster featuring both terminal and triply bridging SbMe₃ ligands; the first example of an unsupported μ₃-organopnictine ligand.

The reaction of [PdCl₂(MeCN)₂] with 2 equiv of SbMe₃Cl resulted in the formation of [PdCl₂(SbMe₃Cl)₂] as a red solid in good yield, which appears stable in air for several hours (Scheme 1). The expected singlet was observed in the ¹H NMR spectrum as well as a single broad ¹³C{¹H} NMR resonance. The solid-state far IR spectrum shows two bands corresponding to Pd–Cl stretches (C₂: A₁ + B₁). Crystals were grown from the benzene filtrate and analyzed by X-ray crystallography. The solid-state structure comprises the centrosymmetric dimeric unit [PdCl₂(SbMe₃Cl)₂]₂, consisting of two distorted square planar Pd centers with cis chloride and chlorostibine ligands, connected by a fairly short Pd(II)–Pd(II) interaction (2.9143(4) Å) (Figure 2).

Most examples of Pd(II) dimers feature bidentate bridging ligands supporting the Pd–Pd interaction. One rare counterexample is the diaminosugar complex [Pd(C₂H₅N₂O₂)Cl₂], (Pd–Pd = 3.284 Å), in which dimerization is supported by H-
bonding between amine and Cl ligands. A similar conformation is adopted by \textsuperscript{[PdCl\textsubscript{4}(SbMe\textsubscript{2}Cl)\textsubscript{2}]}\textsubscript{2}, each chlorostibine ligand eclipses a Cl ligand on the opposite Pd center when viewed down the Pd–Pd vector (torsion angles: Cl4–Pd1–Pd1a–Sb1a = 3.94(3)°, Cl3–Pd1–Pd1a–Sb2a = 5.68(3)°), leading to very short intermolecular Sb–Cl distances (mean 2.96 Å, cf. mean Sb–Cl covalent = 2.39 Å, \(\Sigma_{vdW} = 4.29\) Å).\textsuperscript{16}

The propensity of coordinated Sb or Bi donors to act simultaneously as acceptors, forming intra- or intermolecular “hypervalent” interactions with electronegative atoms, is a current area of interest,\textsuperscript{15} and it has been demonstrated that these interactions can strongly direct the solid-state structure of a complex.\textsuperscript{17} It appears that in \textsuperscript{[PdCl\textsubscript{2}(SbMe\textsubscript{2}Cl)\textsubscript{2}]}\textsubscript{2}, four such Sb···Cl interactions support the formation of the dimeric species. These interactions form approximately \textit{trans} to the covalently bonded halide substituent on Sb (mean \(\angle\) Cl–Sb–Cl = 169.0°), the Sb–Cl \(\sigma^*\) being the most accessible acceptor orbital on Sb. Consistent with this, natural bond orbital (NBO) analysis identifies a notable \(3p_{CI} \rightarrow \sigma^*_{Sb-Cl}\) interaction (see SI for further details). The geometry at Sb is near trigonal bipyramidal, severely distorted from the expected pseudotetrahedral. The structure is reminiscent of that of the Pt(II)–Pt(II) dimer \textsuperscript{[PtCl\textsubscript{4}(S-C\textsubscript{6}H\textsubscript{4}SbMe\textsubscript{2})\textsubscript{2}]}\textsubscript{2}, which contains weak intermolecular Sb···Cl contacts (mean 3.48 Å),\textsuperscript{18} the considerably shorter Sb···Cl distances found in \textsuperscript{[PdCl\textsubscript{4}(SbMe\textsubscript{2}Cl)\textsubscript{2}]}\textsubscript{2} can be accounted for by the increased acceptor power of the halostibine in comparison to the triorganoantimony. In each case it is difficult to separate the magnitude of the secondary Sb···Cl interaction from that of the metallophilic interaction between the group 10 metals.

There are very few previous reports of halostibine complexes with transition metal halides. In view of the recent interest surrounding the “noninnocent” behavior of coordinated stibines, we investigated the reactivity of \textsuperscript{[PdCl\textsubscript{4}(SbMe\textsubscript{2}Cl)\textsubscript{2}]}\textsubscript{2}, with reagents which specifically have the potential to target both the Pd and Sb metal centers. Treatment of \textsuperscript{[PdCl\textsubscript{4}(SbMe\textsubscript{2}Cl)\textsubscript{2}]}\textsubscript{2} with 8 equiv of MeLi (equimolar with Cl) in tetrahydrofuran resulted in the formation of an intensely violet solution, from which a dark purple solid was isolated (Scheme 1). The product is stable over several weeks when stored under an N\(_2\) atmosphere, but slowly becomes black/brown in contact with air. It is remarkably soluble in n-hexane and less soluble in chlorinated solvents. Small purple crystals were analyzed by X-ray diffraction, giving the solid-state structure shown in Figure 3, formulated as \textsuperscript{[Pd\textsubscript{4}(\mu_2-SbMe\textsubscript{3})\textsubscript{4}(SbMe\textsubscript{3})\textsubscript{4}]}\textsubscript{4}.

The structure comprises a central tetrahedron of four Pd(0) atoms, with an average Pd–Pd distance of 2.805 Å. Each Pd is coordinated to one terminal SbMe\textsubscript{3} ligand (mean Pd–Sb = 2.520 Å) and one SbMe\textsubscript{3} ligand caps each face of the tetrahedron, bridging three Pd atoms (mean Pd–Sb = 2.773 Å). A mirror plane bisects the tetrahedron, passing through two Pd atoms, two bridging Sb, and two terminal Sb atoms. There is symmetry-related disorder of the Me substituents on the terminal Sb1. Each bridging SbMe\textsubscript{3} ligand is almost equidistant from the three Pd atoms it caps; the least symmetrical is Sb5, with a difference of 0.07 Å between Sb5–Pd1 and Sb5–Pd2. The most symmetrical, Sb4, has <0.01 Å difference between Sb4–Pd1, Sb4–Pd2, and Sb4–Pd3. The molecule has near C\(_{3v}\) symmetry, but attempts to solve the diffraction data in higher symmetry space groups were unsatisfactory; the Cmc\(_2\) solution is correct. Figure 3b,c shows alternative views of the structure in which this pseudosymmetry can be clearly discerned.

The \textsuperscript{1}H and \textsuperscript{13}C\{\textsuperscript{1}H\} NMR spectra of \textsuperscript{[Pd\textsubscript{4}(\mu_2-SbMe\textsubscript{3})\textsubscript{4}(SbMe\textsubscript{3})\textsubscript{4}]}\textsubscript{4} in benzene-\textit{d}_\textit{6} solution each display two broad resonances of equal intensity, corresponding to two
distinct SbMe₃ environments. This is consistent with the conservation of the tetramer in solution, the broadening of the peaks being most likely due to the proximity of the quadrupolar Sb nuclei (¹²⁹Sb I = 5/2, ¹²⁸Sb I = 7/2). The identity of the product is supported by elemental analysis.

The triply bridging behavior of a monodentate organo-pnictine ligand is unprecedented. Of the two systems previously reported which feature μ₃-pnictines, the first involves PF₅, a strong π-acceptor ligand which can be considered as electronically more akin to CO than to PR₃. In [Pd₃(μ₃-PF₅)(μ-X)(μ-dppm)]. Full geometry optimization under pnictine ligand is unprecedented. Of the two systems previously reported with similar Pd cluster interactions, 27 the formal cluster electron count of 56 for [Pd₄(SbMe₃)₄] is particularly unexpected given that the bridging SbMe₃ is unsupported, i.e., not stabilized by polydentate bridging moieties, and that SbMe₃ might be expected to be only a moderate π-acceptor. The cluster is held together entirely by μ₃-SbMe₃ bridges and Pd−Pd interactions. Comparable Pd(0)₄ clusters with terminal phosphines and μ₂-bridging CO or SO₂ ligands have been reported with similar Pd−Pd distances, though they are generally of lower symmetry. 28,29 Recently, the unusual [[(CNBu)]₄(GaCp*)₄] cluster was reported, containing a highly symmetric Pd₄Ga₄ core, comparable to the Pd₄Sb₄ core of [Pd₄(μ₃-SbMe₃)(SbMe₃)₄], with a similar Pd−Pd distance (2.875 Å) and Pd−Ga distances of 2.535 Å. 31

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NBO calculations demonstrated significant Pn → M donor interactions as well as weaker Pn ← M acceptor interactions, amounting to a symmetrical four-center two-electron bridging PnPnPn interaction.

The structure of [Pd₄(μ₃-SbMe₃)(SbMe₃)₄] is particularly unexpected given that the bridging SbMe₃ is unsupported, i.e., not stabilized by polydentate bridging moieties, and that SbMe₃ might be expected to be only a moderate π-acceptor. The cluster is held together entirely by μ₃-SbMe₃ bridges and Pd−Pd interactions. Comparable Pd(0)₄ clusters with terminal phosphines and μ₂-bridging CO or SO₂ ligands have been reported with similar Pd−Pd distances, though they are generally of lower symmetry. 36,20 Recently, the unusual [[(CNBu)]₄(GaCp*)₄] cluster was reported, containing a highly symmetric Pd₄Ga₄ core, comparable to the Pd₄Sb₄ core of [Pd₄(μ₃-SbMe₃)(SbMe₃)₄], with a similar Pd−Pd distance (2.875 Å) and Pd−Ga distances of 2.535 Å. 31

Density functional theory (DFT) was employed to provide insight into the electronic structure of [Pd₄(μ₃-SbMe₃)(SbMe₃)₄]. Full geometry optimization under C₄ symmetry afforded a structure with bond parameters closely matching the crystal structure. However, to facilitate the analysis, we used a C₄-optimized geometry: this lies only 3 kcal mol⁻¹ above the C₁ minimum.37

The formal cluster electron count of 56 for [Pd₄(μ₃-SbMe₃)(SbMe₃)₄] is 4 electrons fewer than the predicted valence electron count of 60 for a tetrahedron with localized bonding. Such an ideal count is exemplified in [Ni₄(CO)₆(P(C₆H₄CN)₃)₄] (T₄ symmetry), 32 which contains 6 edge-bridging carbonyls and 4 terminal phosphine ligands at the vertices. However, stable electron-deficient clusters are not uncommon for the heavier group 10 metals 38,23−28 which often form stable compounds that do not conform to the 18-electron rule, a fact attributed to the increased energy gap between the valence d and p orbitals in these late transition metals. Mings reported the electronic structure of the hypothetical [Pt(PH₃)₂]₄ clusters, in which terminal PH₃ bonding was assumed, and predicted counts of 56 or 54 electrons depending on the orientation of the ligands. 27

Both the stability and diamagnetism of the title cluster are borne out in the molecular orbital (MO) diagram (Figure S2). There are 40 electrons that occupy all orbitals of the d manifold, forming a band of MOs centered on the edges and faces of the Pd₄ core. Overlap between symmetry-adapted (A₁ + 2e) ligand group donor orbitals with combinations of metal-based σ-type S/Sp cluster acceptor orbitals of matching symmetry leads to the formation of bonding MOs, lying energetically below the d block. These orbitals accommodate the eight donor electron pairs and account for metal−ligand bonding. A considerable gap of ~2 eV separates the LUMO (e₁ symmetry) from the HOMO.

An energy decomposition analysis (EDA) 38,29 was carried out in order to compare the donor−acceptor capabilities of the terminal and face-capping stibine ligands and their interactions with the remaining [Pd₄(SbMe₃)₄] fragment (Table 1). The terminal SbMe₃ ligand exhibits a larger fragment binding energy, −Dₐ (−17.2 kcal mol⁻¹) compared to the face-capping motif (−10.3 kcal mol⁻¹). The face-capping location of the μ₃-SbMe₃ ligand over a [Pd₄] face results in enhanced interactions relative to the terminal SbMe₃ interacting with a single Pd center. Thus, μ₃-SbMe₃ has a larger ∆Eₓtal (47.2 vs +15.5 kcal mol⁻¹), but this is offset by a greater ∆Eorb (−65.5 vs −37.8 kcal mol⁻¹). The individual contributions to ∆Eorb are dominated by the A₁ and E₁ components equating to σ-donation (Sb → Pd) and π-back-donation (Sb ← Pd), respectively; both components are again more significant for the μ₃-SbMe₃ ligand. It is striking that for both binding modes the electrostatic term ∆E stk contributes a significantly larger contribution (71−76%) to the total metal−ligand bonding than the orbital term ∆Eorb (24−29%). A similar observation has been reported for terminal phosphines, 30 indicating that focusing on orbital interactions alone may be misleading.

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Figure S1. Table 1. EDA Results of Cluster [Pd₄(μ₃-SbMe₃)(SbMe₃)₄]₄

| term | terminal | face-capping |
|------|----------|--------------|
| ∆Eₚₐₚ | +133.9 kcal mol⁻¹ | +208.9 kcal mol⁻¹ |
| ∆E₂ₚ₁ | −118.4 kcal mol⁻¹ | −161.7 kcal mol⁻¹ |
| ∆Eₚₜₚ | +15.5 kcal mol⁻¹ | +47.2 kcal mol⁻¹ |
| ∆E₁ₕₐₚ | −37.8 kcal mol⁻¹ | −65.5 kcal mol⁻¹ |
| ∆E₂ₚₜ | −21.8 kcal mol⁻¹ | −32.9 kcal mol⁻¹ |
| ∆E₁ₕₜ | −0.3 kcal mol⁻¹ | −0.8 kcal mol⁻¹ |
| ∆E₁ₚ́ | −15.7 kcal mol⁻¹ | −31.7 kcal mol⁻¹ |
| ∆Eₓₜₚ | −22.3 kcal mol⁻¹ | −18.3 kcal mol⁻¹ |
| ∆Eₓₜₜ | +5.1 kcal mol⁻¹ | +8.0 kcal mol⁻¹ |
| −Dₐ | −17.2 kcal mol⁻¹ | −10.3 kcal mol⁻¹ |
| −Dₐ + dispersion | −45.8 kcal mol⁻¹ | −53.6 kcal mol⁻¹ |

*All energy values in kcal mol⁻¹. Values in parentheses give percentage contributions to the total attractive interactions (ΔEₓtal) and ΔEorb. ∆Eₓtal = ∆Eₚₐₚ + ΔE₂ₚ₁ + ΔEₚₜₚ + ΔE₁ₕₐₚ + ΔE₂ₚₜ + ΔE₁ₕₜ + ΔE₁ₚ́ + ΔEₓₜₚ + ΔEₓₜₜ. ∆Eorb = ΔE₁ₚ́ + ΔE₂ₚₜ + ΔE₁ₕₜ + ΔE₁ₕₚ + ΔEₚₜₚ + ΔE₂ₚ₁ + ΔEₓₜₚ + ΔEₓₜₜ*

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Pd acceptor orbital (5s) makes a strong contribution to bonding ($\Delta E_{orb}^{1} = -14.8$ kcal mol$^{-1}$). Two components of $\pi$-back donation from Pd to Sb can be clearly identified by energies of $\Delta E_{orb}^{2} = \Delta E_{orb}^{3} = -6.0$ kcal mol$^{-1}$. A similar analysis for the $\mu_{3}$-SbMe$_3$ fragment reveals an increase in the stabilization energies and associated charge flows for both the $\pi$ ($\Delta E_{orb}^{1} = -24.5$ kcal mol$^{-1}$) and $\sigma$ channels ($\Delta E_{orb}^{2} = \Delta E_{orb}^{3} = -10.5$ kcal mol$^{-1}$) due to the larger overlap area provided by the Pd$_3$ face, in line with the EDA analysis. To summarize, a rare example of a halostibine complex with a transition metal halide has been synthesized and characterized as a dimer in the solid state, supported by secondary Sb–Cl interactions. This complex demonstrates unexpected reactivity with MeLi, resulting in isolation of a highly unusual Pd(0) cluster with $\mu_{3}$-SbMe$_3$ ligands; the first example of triple bridging by a monodentate organopnictine. Computational modeling of the cluster reveals that both bridging and terminal SbMe$_3$ ligands can be efficient acceptors in metal-to-ligand $\pi$-back donation, helping to stabilize the electron rich [Pd$_3$] core. Investigation of potential phosphine and arsine analogues is underway in our group. The effect of this new pnictine bonding mode on the electronic environment of the transition metal could have considerable impacts in organometallic chemistry, including in the design of new homogeneous catalysts.

**ASSOCIATED CONTENT**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b04060.

Experimental and computational details (PDF)

Crystalllographic data (CIF)

Crystalllographic data (CIF)

Optimized coordinate file (XYZ)

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The authors declare no competing financial interest.

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