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Antimony Diiminopyridine Complexes

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The stoichiometric reactions of antimony trichloride, trimethylsilyl trifluoromethanesulfonate, and diiminopyridine ligands lead to the formation of *N,N',N''*-chelated SbCl₂ cationic complexes. Methyl, phenyl substituents on the imine carbons of the ligand yielded structures with a lone pair on antimony and the hydrogen substituted variant was notably different as it forms a Menshutkin complex with meta-xylene in the solid-state.

Diiminopyridine (DIMPY) ligands have gained attention as pincer ligands with transition metals since their inception in 1960.¹ In comparison to the wealth of reported d-block examples,^{1e, 2} complexation to the p-block elements has been less explored. The majority of the group 13-16 elements have been reported,³ although for group 15, only phosphorus and arsenic have been disclosed.^{3j, 3n, 4} Cowley and coworkers prepared arsenic DIMPY species (**A**, Figure 1) by the reaction of ligand with arsenic triiodide to generate the As(I) cationic complex with an [As₂I₈] dianion or by the 1:1:1 reaction of AsCl₃, SnCl₂, and DIMPY to give the same cationic As(I) species with an [SnCl₅•THF] anion (Figure 1).³ⁿ

Martin and Ragona isolated *N,N',N''*-chelated P(III) cations with an [I₃] anion from the reactions of PI₃ with DIMPY ligands

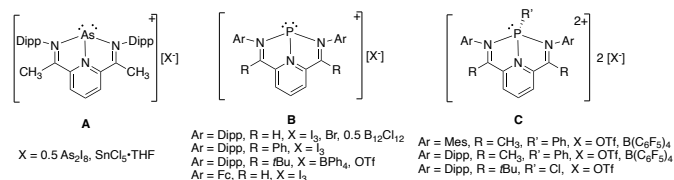


Figure 1: Known arsenic and phosphorus DIMPY complexes. Fc = ferrocene; Mes = 2,4,6-trimethylphenyl; Dipp = 2,6-diisopropylphenyl; OTf = trifluoromethanesulfonate.

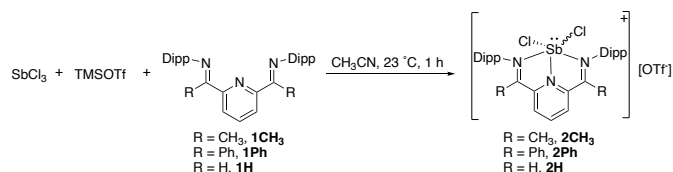
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(**B**, Figure 1).^{3j} The substitution on the α -carbon was important in this case as the phenyl- and hydrogen-substituted ligands resulted in isolable products while the methyl variant produced a complex mixture, a problematic issue in reactions of Schiff base ligands with p-block halide reagents.^{3h, 3m, 4a, 5} Follow up work by the same group and the Herbert group to provide a series of P(III) species of type **B** that feature Dipp (2,6-diisopropylphenyl) of ferrocene on nitrogen; a hydrogen, phenyl, or tert-butyl group on the imine carbon; and varied anions.^{4b, 4c} Stephan, Chitnis, and coworkers as well as Herbert and coworkers accessed phosphorus(III) DIMPY dications by reacting DIMPY ligands with PhPCl₂ and a halide abstracting agent in a one-pot reaction (**C**).^{4a, 4b} In this work, we report the first reactions of DIMPY ligands with an antimony reagent.

The 1:1:1 stoichiometric reactions of antimony(III) chloride with diiminopyridine ligands bearing 2,6-diisopropylphenyl groups (Dipp) on the imine nitrogen and varying substituents on the α -carbon (R = CH₃, **1CH₃**; R = Ph, **1Ph**; R = H, **1H**) and trimethylsilyl trifluoromethanesulfonate (TMSOTf) were conducted at room temperature (Scheme 1). Proton NMR spectroscopy indicated conversion for all reactions within an hour. All three complexes were isolated in quantitative yield as yellow (**2CH₃**), red (**2Ph**), and orange solids (**2H**) after removal of solvent and the TMSOTf byproduct in vacuo. In reactions with **1CH₃** and **1H**, the shift of the substituent on the α -carbon is diagnostic with downfield shifts from the free ligand [**2CH₃**: 2.77 ppm c.f. **1CH₃**: 2.29 ppm; **2H**: 9.22 ppm c.f. **1H**: 8.34 ppm].⁶ In the reaction with **1Ph**, the ¹H NMR spectrum of the product contains signals consistent with a locked configuration in comparison to the restricted rotation at room temperature for the free ligand.⁷ The *meta*-protons of the pyridine ring are



Scheme 1: Synthesis of antimony complexes **2CH₃**, **2Ph**, and **2H**.

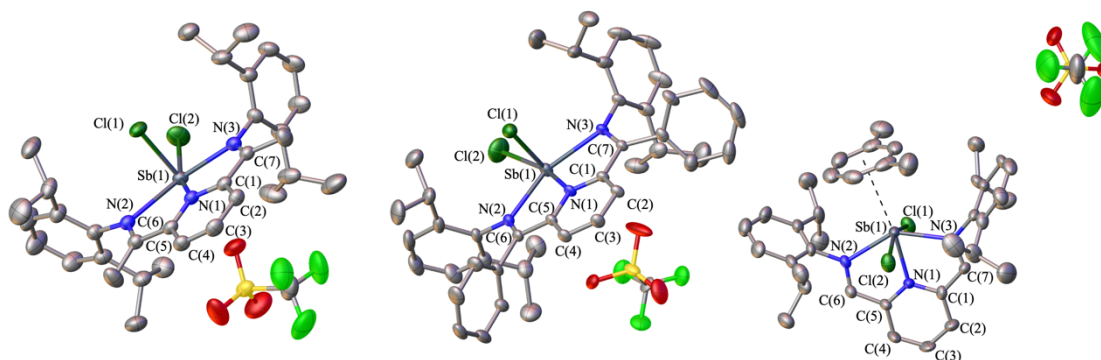


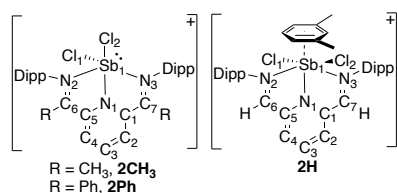
Figure 2: Solid-state structures of **2CH₃**, **2Ph**, and **2H** (left to right). Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms and non-coordinating solvent molecules are omitted for clarity. In species with disorder, only the major component is shown.

chemically equivalent in all species, consistent with symmetric chelation. In the ¹⁹F NMR spectra, singlets were observed in the ionic region for triflate anions [**2CH₃**: -79.2 ppm, **2Ph**: -79.1 ppm, **2H**: -79.2 ppm, c.f. -78.3 to -78.9 ppm for phosphorus DIMPY complexes **B** and **C** with triflate counter anions, Figure 1, and covalent CH₃OTf = -76.3 ppm].^{4a, 4b, 8}

Single-crystal X-ray diffraction studies on crystals grown revealed their identities as the κ³-N,N',N''-chelated SbCl₂ cationic complexes **2** with a non-bound triflate counter anion (Figure 2, Table 1). The molecular geometry of **2CH₃** and **2Ph** are both square pyramidal with a chloride trans to the pyridine nitrogen. The chloride trans [Cl(1)] to the pyridine nitrogen has a longer Sb-Cl bond than the cis chloride [Cl(2)] rationalized by

the trans effect of the pyridyl nitrogen atom in comparison to the lone pair, resulting in elongation [Table 1; **2CH₃**: Sb-Cl(1) = 2.5218(6) Å, Sb-Cl(2) = 2.3560(6) Å; **2Ph**: Sb-Cl(1) = 2.5224(12) Å, Sb-Cl(2) = 2.3619(11) Å]. Despite the ligand having symmetry in the NMR spectra, in the solid state, the two Sb-N bonds to the imine nitrogens are notably closer to one nitrogen than the other [**2CH₃**: Sb-N(2) = 2.4925(18) Å, Sb-N(3) = 2.3002(18) Å; **2Ph**: Sb-N(2) = 2.310(3) Å, Sb-N(3) = 2.545(3) Å]. The apparent symmetry in solution, as inferred from the ¹H NMR spectra, suggests that bond-no bond resonance between the imine N's and the Sb center is occurring in solution for **2CH₃** and **2Ph**. This dynamic scaffold phenomenon has been observed in pnictogen complexes with N_{imine}CN_{imine} pincer ligands.⁹

Table 1: Salient bond lengths and angles of cations in **2CH₃**, **2Ph**, and **2H**.



	2CH₃	2Ph	2H
Sb(1)-N(1)	2.3294(17) Å	2.308(3) Å	2.201(4) Å
Sb(1)-N(2)	2.4925(18) Å	2.310(3) Å	2.379(4) Å
Sb(1)-N(3)	2.3002(18) Å	2.545(3) Å	2.363(4) Å
Sb(1)-Cl(1)	2.5281(6) Å	2.5224(12) Å	2.5521(13) Å
Sb(1)-Cl(2)	2.3560(6) Å	2.3619(11) Å	2.4844(14) Å
C(1)-N(1)	1.336(3) Å	1.343(4) Å	1.348(7) Å
C(5)-N(1)	1.342(3) Å	1.342(4) Å	1.338(7) Å
C(6)-N(2)	1.279(3) Å	1.295(4) Å	1.258(6) Å
C(7)-N(3)	1.287(3) Å	1.287(4) Å	1.278(7) Å
C(1)-C(7)	1.488(3) Å	1.484(4) Å	1.455(8) Å
C(5)-C(6)	1.488(3) Å	1.483(5) Å	1.467(7) Å
C(1)-C(2)	1.393(3) Å	1.390(4) Å	1.407(8) Å
C(2)-C(3)	1.385(3) Å	1.396(5) Å	1.389(10) Å
C(3)-C(4)	1.380(3) Å	1.388(5) Å	1.369(9) Å
C(4)-C(5)	1.396(3) Å	1.389(5) Å	1.385(8) Å
Cl(1)-Sb(1)-Cl(2)	85.74(2)°	85.74(5)°	155.88(5)°
N(1)-C(5)-C(6)	116.17(17)°	115.8(3)°	115.1(5)°
N(1)-C(1)-C(7)	115.64(17)°	116.7(3)°	116.3(5)°
C(5)-C(6)-N(2)	115.60(19)°	118.9(3)°	119.3(5)°
C(1)-C(7)-N(3)	117.40(19)°	116.8(3)°	118.2(5)°

In the solid state structure of **2H**, the molecular geometry is octahedral with the site trans to the pyridine occupied by a meta-xylene, such species are colloquially known as Menshutkin complexes.^{10,11} The antimony distance to the centroid of the ring is 3.418 Å which lies in the range of reported Menshutkin complexes (3.04-4.17 Å).¹² This interaction results in an increase in symmetry about the antimony center in **2H** with Sb-N_{imine} bonds that are much closer in magnitude [Sb-N(2) = 2.379(4), Sb-N(3) 2.363(4) Å] as well as the Sb-Cl bonds [Sb-Cl(1) = 2.5521(13) Å, Sb-Cl(2) 2.4844(14) Å].

The synthesized N,N',N''-chelated antimony(III) DIMPY complexes represent the first examples of antimony DIMPY complexes. The solid state crystal structures were analyzed, and the species bearing hydrogen on the imine carbon adopted a Menshutkin complex exhibiting a weak interaction with aromatic solvent identified by X-ray crystallography.

Conflicts of interest

The authors declare no conflict of interests.

Acknowledgements

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