

An electrophilic, intramolecularly base-stabilized platinum-antimony complex

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ABSTRACT: As part of our interest in the chemistry of late transition metal complexes bearing cationic antimony ligands, we have investigated the reaction of $((o\text{-(Ph}_2\text{P)C}_6\text{H}_4)_3\text{SbClPtCl}$ (**1**) with H_2O_2 and found that it affords $[((o\text{-(Ph}_2\text{P)C}_6\text{H}_4)_2(o\text{-(Ph}_2\text{PO)C}_6\text{H}_4)\text{SbPtCl}]^+$ (**[2-Cl]**⁺), a monocationic complex with the newly installed P=O moiety coordinated intramolecularly to the antimony atom via a P=O→Sb dative bond aligned with the Sb-Pt axis. The Pt-Cl bond of this complex is readily activated by addition of a ligand such as cyclohexyl isocyanide. When carried out in the presence of AgBF_4 , this reaction affords the dicationic complex $[((o\text{-(Ph}_2\text{P)C}_6\text{H}_4)_2(o\text{-(Ph}_2\text{PO)C}_6\text{H}_4)\text{SbPt(CNCy)}]^+$ (**[2-CNCy]**²⁺). In addition to structurally characterizing **[2-Cl]**⁺ and **[2-CNCy]**²⁺ as their chloride and tetrafluoroborate salts, respectively, we have also studied the reaction of **[2-Cl]**⁺ with AgBF_4 in the presence of PhCCH as a substrate surrogate. When monitored by ^{31}P NMR spectroscopy in CDCl_3 , this reaction shows the formation of a new species tentatively assigned to $[((o\text{-(Ph}_2\text{P)C}_6\text{H}_4)_2(o\text{-(Ph}_2\text{PO)C}_6\text{H}_4)\text{SbPt}]^{2+}$ (**[2]**²⁺) stabilized by coordination of the alkyne. This formulation is supported by the elevated carbophilic reactivity of **[2]**²⁺ which readily catalyzes the cyclization of 2-allyl-2-(2-propynyl)malonate. Altogether, these results show that the accumulation of charge in such reactive complexes can be facilitated by the intramolecular base-stabilization of the dinuclear core.

INTRODUCTION

While often considered as mimicking the properties of phosphine and arsine ligands, a number of recent investigations have shown that stibine ligands possess a number of distinguishing qualities that differentiate them from their lighter analogs.¹ Indeed, owing to the larger size of antimony and its higher Lewis acidity, the antimony atom of metal-coordinated stibines has been shown to engage electron rich entities, in particular anions as illustrated in Chart 1 which shows that donor coordination to the antimony atom can occur trans from the metal center (**A**) or trans to one of the antimony-bound substituents (**B**).² This last point can be further illustrated by the structure of $[\text{PdCl}_2(\text{SbMe}_2\text{Cl})_2]_2$ which adopts a dimeric structure supported by Cl→Sb contacts (Chart 1).³ Such a behavior illustrates the coordination non-innocence of metal-bound stibine ligands, a trait that we have exploited for applications in anion sensing.⁴ Given our interest in late transition metal catalysis,⁵ we have now started to question whether the donor stabilization of a metal bound stibine could provide a handle over the stabilization of electron deficient species. We first tested this idea by investigating the coordination of the tris(phosphino)stibine ligand **L**⁶ to gold, followed by the selective oxidation of one of the three phosphino groups.⁷ These efforts resulted in the generation of the cationic complex **[C]**²⁺, with the newly formed phosphine-oxide functionality stabilizing the polycationic heterobimetallic core by coordination to the antimony atom (Chart 1). To build on these earlier results, we have now decided to test if this intramolecular base stabilization strategy could also be used to access related electrophilic platinum complexes. In this contribution, we describe our efforts towards this goal based on the oxidation of the known divalent platinum lantern complex **1-Cl**₂ formed by reaction of **L** with PtCl_2 .⁸

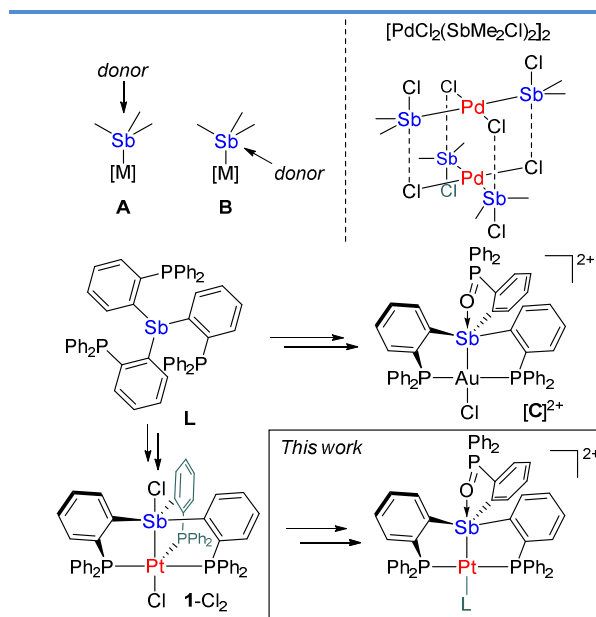


Chart 1. Lewis acidic behavior of coordinated stibines and examples of palladium-, platinum- and gold-antimony complexes. The inset shows the type of structures targeted in this study.

RESULTS AND DISCUSSION

To explore the abovementioned idea, complex **1-Cl**₂ was allowed to react with H_2O_2 in CH_2Cl_2 . Monitoring this reaction by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy indicated rapid consumption of the starting material **1-Cl**₂ and formation of a new species (**[2-Cl]**⁺) characterized by two resonances at 31.8 ppm and 56.0 ppm (Figure 1). Integration of this spectrum indicates a 1:2 ratio consistent with a structure featuring two phosphine arms coordinated to the platinum center and one phosphine oxide functionality. In support of this

assignment, we note that the signal at 56.0 ppm, corresponding to the platinum-bound phosphines, is coupled to the ^{195}Pt nucleus by $^1J_{\text{Pt-P}} = 2635$ Hz. Both the $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shift of this resonance and its scalar coupling to platinum are close to those of $[(o\text{-(Ph}_2\text{P)C}_6\text{H}_4)_2\text{SbCl}_2]\text{PtCl}$ (56.0 ppm, $^1J_{\text{Pt-P}} = 2566$ Hz).⁹ The phosphine oxide resonance at 31.8 ppm does not show any coupling to platinum and comes at a chemical shift value

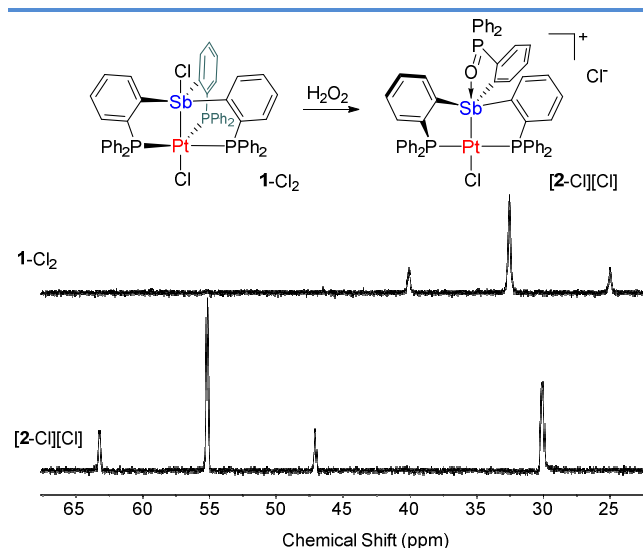


Figure 1: Synthesis of $[\mathbf{2}\text{-Cl}][\text{Cl}]$ and corresponding NMR spectra collected for the in situ reaction before and after addition of H_2O_2 .

very close to that of Ph_3PO (29.6 ppm). The similarity of these two resonances suggests that the $\text{P}=\text{O}$ functionality of $[\mathbf{2}\text{-Cl}][\text{Cl}]$ is not experiencing significant electrophilic activation through $\text{P}=\text{O} \rightarrow \text{Sb}$ bonding¹⁰ as observed in $[\text{Ph}_3\text{Sb}(\text{OPPh}_3)_2]^{2+}$ or $[\mathbf{C}]^{2+}$ which display $\text{P}=\text{O}$ resonances at 42.3 ppm and 48.40 ppm, respectively.^{7, 11}

To more precisely assess the structure of $[\mathbf{2}\text{-Cl}][\text{Cl}]$, we decided to grow single crystals of this derivative by diffusion of Et_2O into a CHCl_3 solution of $[\mathbf{2}\text{-Cl}][\text{Cl}]$. An X-ray diffraction study of these crystals confirm the oxidation of one of the three phosphine moieties of the starting complex and formation of a monocationic complex (Figure 2). Indeed, the chloride anion formerly bound to the antimony center of the starting material now sits in the lattice where it forms hydrogen bonds with two interstitial CHCl_3 molecules. Inspection of the structure of the cationic platinum antimony complex shows that the newly formed phosphine oxide functionality is coordinated to the antimony atom, as confirmed by the O-Sb distance of 2.432(4) Å. This bond is significantly longer than those reported for $[\text{Ph}_3\text{Sb}(\text{OPPh}_3)_2]^+$ (av. 2.102(2) Å)¹¹ and $[\mathbf{C}]^{2+}$ (2.206(7) Å),⁷ pointing the weakness of the $\text{P}=\text{O} \rightarrow \text{Sb}$ interaction in $[\mathbf{2}\text{-Cl}][\text{Cl}]$. Nonetheless, formation of this interaction is accompanied by displacement of the antimony-bound chloride anion present in $\mathbf{1}\text{-Cl}_2$. It follows that compound $[\mathbf{2}\text{-Cl}][\text{Cl}]$ is a salt consisting of a cationic platinum antimony complex and a chloride counter anion that does not appear to be involved in any short contacts, except with a solvate chloroform molecule. Further inspection of the structure of $[\mathbf{2}\text{-Cl}][\text{Cl}]$ indicates that the antimony center adopts a distorted trigonal bipyramidal geometry with the phosphine oxide and the platinum atom positioned at the apical sites, resulting in a O-Sb-Pt angle of 178.15(11)°. The three equatorial positions are occupied by the three phenylene linkers of the ligand backbone. The sum of the resulting $\text{C}_{\text{Ar}}\text{-Sb-C}_{\text{Ar}}$ angles is equal to 351.6° indicating a noticeable deviation from the ideal value of 360°. As a result of this deviation, the antimony center sits 0.36 Å below the plane defined by the three ipso carbon atoms. This structural feature suggest that $[\mathbf{2}\text{-Cl}]^+$ could also be regarded as containing a platinum-bound stibine ligand stabilized by a secondary interaction with the phosphine oxide donor.^{2a} The platinum center adopts a square planar geometry with the chloride coordinating trans to the antimony

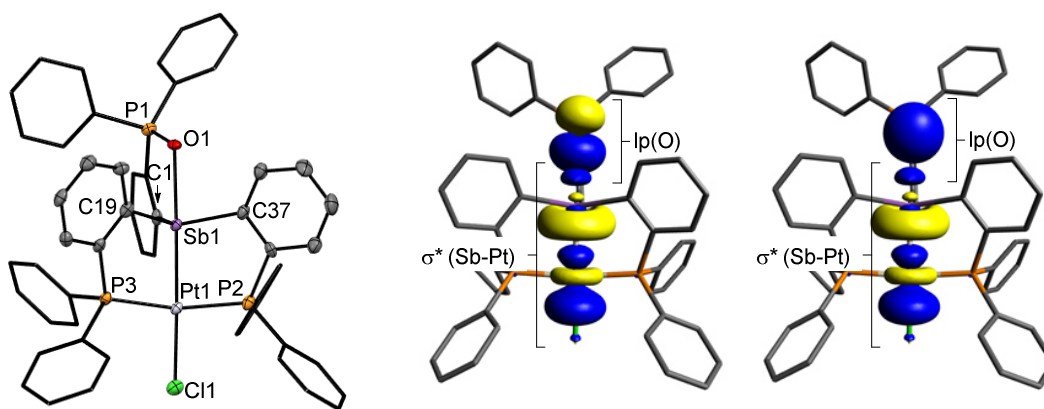


Figure 2: Left: Solid state structure of $[\mathbf{2}\text{-Cl}][\text{Cl}]$. Thermal ellipsoids are drawn at a 50% probability level. The phenyl groups are drawn in wireframe, the hydrogen atoms, interstitial solvent molecules, and counteranion are omitted for clarity. Relevant parameters may be found in the text. Right: NBO plots of Sb-Pt and O-Sb major bonding interactions computed for $[\mathbf{2}\text{-Cl}]^+$.

center. The Sb-Pt bond distance of 2.5247(6) Å is comparable to that found in $[(o\text{-(Ph}_2\text{P)C}_6\text{H}_4)_2(\text{Ph})\text{SbClPtCl}]$ (2.5380(8) Å), a related complex that lacks a phosphine-

oxide functionality.¹² The similarity of these bond lengths suggests that the displacement of the antimony-bound

chloride anion in $[2\text{-Cl}][\text{Cl}]$ by the phosphine-oxide does not notably affect the core of the complex.

The structure of $[2\text{-Cl}][\text{Cl}]$ has also been studied computationally using DFT methods. The optimized geometry resulting from these calculations is in good agreement with those experimentally determined although the computed O-Sb distance is elongated by 0.11 Å when compared to that in the crystal. This optimized geometry was subsequently used to carry out an NBO analysis which indeed indicates donation of two oxygen lone pairs into the Sb-Pt σ^* orbital (Figure 2). These $\text{lp}(\text{O}) \rightarrow \sigma^*(\text{Sb-Pt})$ interactions contribute 33.9 kcal/mol to the stability of the molecule as indicated by a deletion calculation. The Lewis acidity of the antimony center also benefits from the presence of C-Sb σ^* orbitals also involved in donor-acceptor bonding with the oxygen lone pairs (see SI). The main $\text{lp}(\text{O}) \rightarrow \sigma^*(\text{Sb-Pt})$ interaction is shown in Figure 2. It is associated to a second order perturbation energy $E(2)$ of 8.8 kcal/mol which is significantly lower than the value of 69.7 kcal/mol calculated for $[\text{C}]^{2+}$ at the same level of theory.⁷ This finding is consistent with the relatively long O-Sb bond distance observed in $[2\text{-Cl}][\text{Cl}]$. The relatively weak O \rightarrow Sb interaction revealed by these calculations suggest that the ionization of the Sb-Cl bond may also be driven by steric effects.

To test the lability of the chloride anion bound to platinum in $[2\text{-Cl}][\text{Cl}]$, we treated the complex with an excess of cyclohexyl isocyanide (CyNC), a ligand that has been shown to displace platinum-bound chloride anions.^{5e} Immediately following treatment with cyclohexyl isocyanide, a new species ($[3][\text{Cl}]_2$) emerged in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum as indicated by the appearance of two new resonances at 45.5 ppm and 30.8 ppm that continue to adhere to a 2:1 intensity ratio (Figure 3). The low-field signal, which corresponds to the platinum-bound phosphines, features satellites separated by $^1J_{\text{Pt-P}} = 2582$ Hz. This coupling constant is analogous to that in $[2\text{-Cl}][\text{Cl}]$, suggesting only moderate disruption of the coordination environment around the divalent platinum center. The presence of an isocyanide ligand is confirmed by an IR band at $\nu_{\text{NC}} = 2229$ cm^{-1} . This new complex proved difficult to isolate in an analytically pure form. With the aim to verify the core structure of $[2\text{-CNCy}]^{2+}$, we decided to generate the tetrafluoroborate salt instead. To this end, $[2\text{-Cl}][\text{Cl}]$ was treated in one pot with two equivalents of AgBF_4 and an excess of cyclohexyl isocyanide. The integrity of the core was immediately evident from the observation of the expected $^{31}\text{P}\{^1\text{H}\}$ NMR resonances at 50.7 ppm ($^1J_{\text{Pt-P}}$

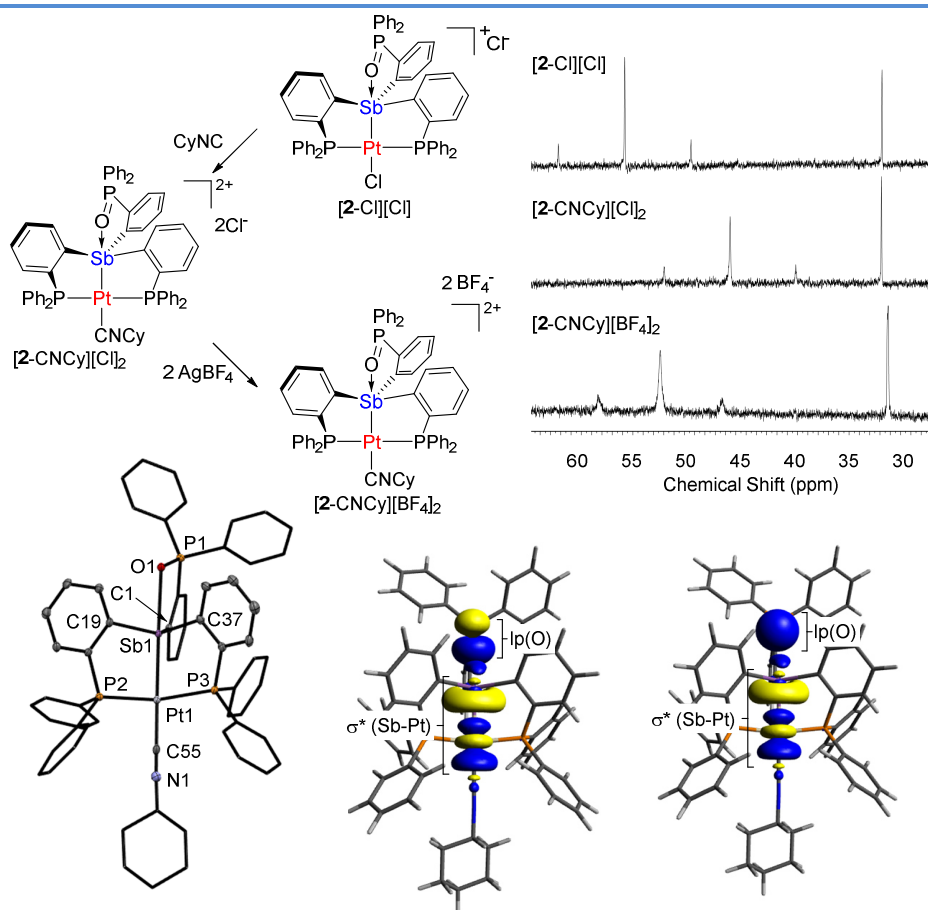
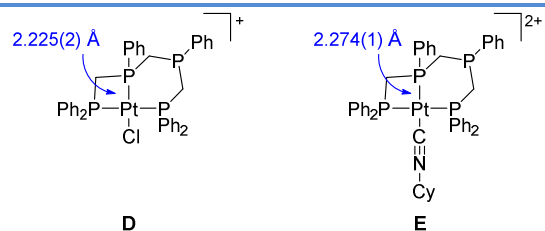


Figure 3: Top: reaction of $[2\text{-Cl}][\text{Cl}]$ with cyclohexyl isocyanide and AgBF_4 . The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra show the formation of $2\text{-CNCy}][\text{Cl}]_2$ and $[2\text{-CNCy}][\text{BF}_4]_2$. Bottom left: Solid state structure of $[2\text{-Cl}][\text{Cl}]$. Thermal ellipsoids are drawn at the 50% probability level. The phenyl groups are drawn in wireframe, the hydrogen atoms, interstitial solvent molecules, and counteranions are omitted for clarity. Bottom right: NBO plots of the major O-Sb bonding interactions.

= 2464 Hz) and 30.4 ppm. The presence of the isocyanide ligand was confirmed by ^1H NMR spectroscopy as well as IR spectroscopy ($\nu_{\text{NC}} = 2232\text{ cm}^{-1}$). The energy of the isocyanide is significantly higher than that of the free ligand ($\nu_{\text{NC}} = 2137\text{ cm}^{-1}$), consistent with the fact that the isocyanide ligand in these complexes serves primarily as a σ -donor.

Single crystals of $[\mathbf{2}\text{-CNCy}][\text{BF}_4]_2$ could be obtained by diffusion of Et_2O into a solution of the complex in CH_2Cl_2 . X-ray crystallography data confirms that the product of this reaction is a dicationic isocyanide platinum complex that does not form any abnormally short contacts with the two BF_4^- counteranions (Figure 3). The core structure of $[\mathbf{2}\text{-CNCy}]^{2+}$ resembles that of $[\mathbf{2}\text{-Cl}]^+$ in $[\mathbf{2}\text{-Cl}][\text{Cl}]$, at the only difference that the platinum-bound chloride of $[\mathbf{2}\text{-Cl}]^+$ is now replaced by a cyclohexyl isocyanide ligand. The resulting Pt-C distance of $2.000(3)\text{ \AA}$ is comparable to that observed in previously studied complexes with similar ligands.^{5e, 8} The square planar platinum center forms a Sb-Pt bond of $2.5684(3)\text{ \AA}$ which is also longer than that in $[\mathbf{2}\text{-Cl}]^+$ ($2.5247(6)\text{ \AA}$). This slight elongation suggests that the neutral cyclohexyl isocyanide ligand has a stronger trans influence than the anionic chloride ligand. While we have not found a clearly stated precedent for this interpretation,



related observations have been made in the case of complexes **D** and **E** recently described by Tanase et al who observed that displacement of the platinum-bound chloride by a cyclohexyl isocyanide ligand leads to a noticeable lengthening of the Pt-P bond trans from the isocyanide ligand.¹³ The phosphine oxide functionality remains coordinated to the antimony center, as indicated by an O-Sb separation of $2.543(2)\text{ \AA}$ which only slightly exceeds that of $[\mathbf{2}\text{-Cl}]^+$ ($2.432(4)\text{ \AA}$). The structure of the dicationic complex $[\mathbf{2}\text{-CNCy}]^{2+}$ was also computationally optimized using the same method and level of theory as that in the case of $[\mathbf{2}\text{-Cl}]^+$. The optimized geometry is again in good agreement with that

determined experimentally while NBO calculations shows that the stabilization provided by the $\text{lp}(\text{O}) \rightarrow \sigma^*(\text{Sb-Pt})$ interactions ($E_{\text{del}} = 30.54\text{ kcal/mol}$) remains close to that calculated for $[\mathbf{2}\text{-Cl}]^+$ (Figure 3).

To conclude this study, we decided to investigate the carbo-philic reactivity of $[\mathbf{2}\text{-Cl}][\text{Cl}]$ upon activation with two equivalents of AgBF_4 . To provide comparative data, we also decided to compare this system to that based on **1-Cl**₂ and two equivalents of AgBF_4 . As a prelude to these studies, we first decided to monitor the reaction of **1-Cl**₂ and $[\mathbf{2}\text{-Cl}][\text{Cl}]$ with AgBF_4 using NMR spectroscopy, in the presence of phenyl acetylene in order to mimic the presence of an alkyne-containing reaction substrate. Addition of two equivalents of the silver activator to a CD_2Cl_2 solution of **1-Cl**₂ led to a spectrum that displays two broad resonances. The downfield resonance at 41.3 ppm shows coupling to the platinum nucleus ($^1J_{\text{Pt-P}} = 2289\text{ Hz}$), which based on signal integration, indicates that two phosphines remain bound to the platinum atom (Figure 4). Interestingly the upfield signal at 14.2 ppm is split into a doublet ($^1J_{\text{Ag-P}} = 650\text{ Hz}$) suggesting, based on the value of the coupling constant, coordination of a silver(I) unit.¹⁴ These spectroscopic features are best reconciled by considering the decoordination of one of the three phosphine arms of **1-Cl**₂ from the platinum center and its coordination to a silver(I) center. The breadth of the resonances also suggests that the three phosphine arms are in rapid exchange. Upon cooling to -40°C , the spectrum splits into two set of resonances consistent with the existence of two species. While the identity of these two species has not been elucidated, the observed signal multiplicity indicates that both a platinum and silver fragment remain coordinated to the phosphine arms of the ligand. These spectra indicate that **1-Cl**₂ does not undergo a simple activation of the Sb-Cl and Pt-Cl bond as originally anticipated. Instead, the silver activator remains coordinated to the liberated phosphine arm and possibly to the platinum atom.¹⁵ When the same experiment was carried out with $[\mathbf{2}\text{-Cl}][\text{Cl}]$ in CD_2Cl_2 , a much simpler process was observed since $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy showed the unambiguous formation of a new species characterized by a phosphine resonance at 52.9 ppm ($^1J_{\text{Pt-P}} = 2442\text{ Hz}$) which is $\sim 3.2\text{ ppm}$ upfield from that of $[\mathbf{2}\text{-Cl}][\text{Cl}]$ (56.1 ppm) (Figure 4) and a phosphine oxide resonance at 30.1 ppm.

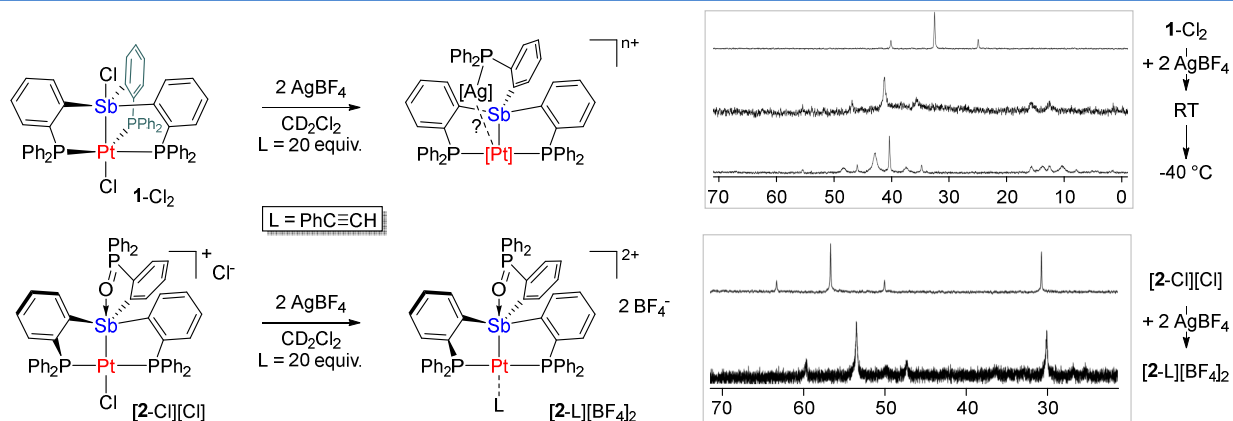
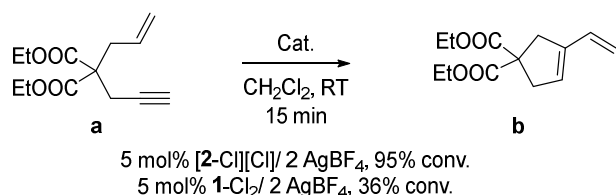


Figure 4: Activation of **1-Cl**₂ (top) and $[\mathbf{2}\text{-Cl}][\text{Cl}]$ (bottom) with two equiv. of AgBF_4 in the presence of phenylacetylene in CD_2Cl_2 . The corresponding $^{31}\text{P}\{^1\text{H}\}$ NMR spectra are shown in the inset. The values on the x-axis are in ppm.



Scheme 1: Enyne cyclization reaction used to benchmark the catalytic activity of the complexes of $1\text{-Cl}_2/2 \text{ AgBF}_4$ and $[2\text{-Cl}][\text{Cl}]/2 \text{ AgBF}_4$.

The spectroscopic features suggest that this new species is the bis(tetrafluoroborate) salt $[2][\text{BF}_4]_2$, stabilized by coordination of the alkyne to the platinum center. While we have not been able to isolate this new cationic complex, we found that it persisted for several hours in solution. To further support the clean activation of $[2\text{-Cl}][\text{Cl}]$, we have also tested the addition of tetrahydrothiophene (tht), after addition of the silver activator. The spectra collected are consistent with the formation of $[2\text{-tht}][\text{BF}_4]_2$ (see Figure S12). Encouraged by these results, we decided to use the cycloisomerization of 2-allyl-2-(2-propynyl)malonate (**a**) as a test reaction (Scheme 1). This reaction was chosen because it has been previously used to benchmark the electrophilic properties of platinum catalysts.^{5e, 5g, 16} We found that **a** was readily isomerized at room temperature to afford **b** when in the presence of $[2\text{-Cl}][\text{Cl}]/2 \text{ AgBF}_4$. Indeed, under these conditions, the reaction proceeded to a conversion greater than 95% in the first 10 minutes. Under the same conditions, $1\text{-Cl}_2/2 \text{ AgBF}_4$ was significantly less active with a conversion of 36% in the same time frame. We speculate that the catalyst emanating from the activation of 1-Cl_2 is less active because coordination of silver to one of the three phosphine impedes activation of the platinum center. The activity of $[2\text{-Cl}][\text{Cl}]/2 \text{ AgBF}_4$ is reminiscent of that displayed by $[(o\text{-(Ph}_2\text{P)C}_6\text{H}_4)_2\text{SbOTf}_2]\text{PtOTf}$ which also promotes such enyne cyclization reactions in just a few minutes when used at a 5% loading.¹⁷ The same reaction was >95% complete after 60 minutes when in the presence of *in situ* generated $[2][\text{BF}_4]_2$ with a loading of 1%.

CONCLUSION

This work advances our understanding of lantern complexes such as 1-Cl_2 in several ways. First, our observation shows that such complexes are amenable to the selective oxidation of one of the phosphino arms which can be converted into a phosphine-oxide without compromising the integrity of the rest of the structure. A second finding is that the newly installed phosphine-oxide functionality readily displaces the antimony bound chloride to afford $[2\text{-Cl}]^+$ as a chloride salt. This spontaneous ionization, driven by both steric effects and the formation of an intramolecular $\text{P}=\text{O} \rightarrow \text{Sb}$ interaction, allows to build up charge on the dinuclear core thus providing a strategy for increasing the electrophilic character of this compound. Another important aspect of this work is the finding that $[2\text{-Cl}]^+$ can be

converted into dicationic complexes as illustrated by the isolation of the isocyanide complex $[2\text{-CNCy}]^{2+}$. In situ experiments also suggest that $[2\text{-L}]^{2+}$ can be generated in the presence of phenylacetylene that plays the role of the stabilizing L ligand. Finally, our results suggest that such dicationic complexes act as catalysts for the cycloisomerization of 2-allyl-2-(2-propynyl)malonate. These results highlight the benefits that may result from the introduction of a phosphine oxide functionality which can drive the accumulation of positive charge via coordination to the antimony center.

EXPERIMENTAL SECTION

General information *cis*- $\text{PtCl}_2(\text{Et}_2\text{S})_2$ and compound 1-Cl_2 were prepared according to the reported procedures.^{8, 18} Solvents were dried by reflux under N_2 over Na/K (pentane, Et_2O) and CaH_2 (CH_2Cl_2 , CD_2Cl_2 and CDCl_3). All other solvents were used as received. Commercially available chemicals were purchased and used as provided (Commercial sources: Fisher Chemical for CyNC, Aldrich for SbCl_3 ; Matrix Scientific for AgBF_4). Ambient temperature NMR spectra were recorded on a Varian Unity Inova 500 FT, a Bruker Avance 500 NMR spectrometer and a Bruker Ascend 400 NMR spectrometer. Variable temperature spectra were recorded on Varian 500 VnmrS instrument. IR spectra were recorded on a Shimadzu IRAffinity-1 FT-IR spectrometer. ^1H and ^{13}C NMR chemical shifts are given in ppm and are referenced against SiMe_4 using residual solvent signals used as secondary standards. ^{19}F NMR chemical shifts are given in ppm and are referenced against CFCl_3 using $\text{BF}_3 \cdot \text{Et}_2\text{O}$ as an external secondary standard with δ -153.0 ppm. Elemental analyses were performed at Atlantic Microlab (Norcross, GA).

Computational Details. Density functional theory (DFT) structural optimizations were performed starting from the solid state structures of complexes $[2\text{-Cl}][\text{Cl}]$ and $[2\text{-CNCy}]^{2+}[\text{BF}_4]_2$ using the Gaussian 09 program.¹⁹ The optimizations were carried out using the BP86 functional, the PCM solvation model with acetonitrile as a solvent and the following mixed basis set: Sb/Pt: cc-pVTZ-PP; P/O/Cl: 6-31g(d'); H/C: 6-31g. Frequency calculations were used to confirm that optimization had converged to true minima. The optimized structures (available as xyz files submitted as supporting electronic information), which are in excellent agreement with the solid-state structures, were subjected to a Natural Bond Orbital (NBO) analysis using the NBO6 program. The resulting NBOs and Natural Localized Molecular Orbitals (NLMOs)²⁰ were visualized and plotted using the Avogadro program (version 1.2.0).²¹

Crystallographic Measurements. The crystallographic measurements for $[2\text{-Cl}][\text{Cl}]$ and $[2\text{-CNCy}][\text{BF}_4]_2$ were performed at 110(2) K using a Bruker APEX-II CCD area detector diffractometer (Mo- K_α radiation, $\lambda = 0.71069 \text{ \AA}$). In each case, a specimen of suitable size and quality was selected and mounted onto a nylon loop. The structures were solved by direct methods, which successfully located most of the non-hydrogen atoms. Semi-empirical absorption corrections were applied. Subsequent refinement on F^2 using the SHELXTL/PC package (version 6.1) allowed location of the remaining non-hydrogen atoms.

Synthesis of [2-Cl][Cl]: A CH₂Cl₂ solution (20 mL) of complex 1 (750 mg, 0.640 mmol) was treated with one equivalent of 30% (v/v) H₂O₂ in water (70 μ L, 0.685 mmol). The resulting mixture underwent a color change from orange to yellow and then colorless upon stirring overnight at room temperature. The reaction solution was then evaporated to afford a light-yellow residue which was taken up in CH₂Cl₂ (5 mL) and precipitation was induced by addition of Et₂O (15 mL). The precipitate was washed with cold Et₂O (2 \times 15 mL) and dried under vacuum. This procedure afforded [2-Cl][Cl] in a crude yield of 78.9% (600 mg, 0.505 mmol). Single crystals of [2-Cl][Cl]·4(CHCl₃) used for X-ray diffraction and elemental analysis were obtained by vapor diffusion of Et₂O (10 mL) into a solution of [2-Cl][Cl] (30 mg, 0.0253 mmol) in CHCl₃ (2 mL) at room temperature. This recrystallization afforded [2-Cl][Cl]·4(CHCl₃) in 26.1% (11 mg, 0.007 mmol). ¹H NMR (499.42 MHz; CD₂Cl₂): δ 8.97 (d, J_{H-H} = 7.4 Hz, 2H, *o*-SbC₆H₄), 7.63–7.70 (m, 2H), 7.57–7.63 (m, 3H), 7.56–7.43 (m, 15H), 7.34–7.43 (m, 10H), 7.1–7.33 (m, 9H), 6.72 (t, J_{H-H} = 7.8 Hz, 1H). ¹³C{¹H} NMR (125.58 MHz; CD₂Cl₂): δ 142.7 (t, J_{C-P} = 35.5 Hz), 137.1 (m), 136.1 (m), 135.2 (s), 134.5 (m), 133.4 (t, J_{C-P} = 13.5 Hz), 133.1 (t, J_{C-P} = 2.7 Hz), 131.8 (m), 131.5 (s), 131.2 (m), 130.8 (s), 130.6 (s), 129.7 (d, J_{C-P} = 276.1 Hz), 128.2 (m), 127.9 (t, J_{C-P} = 11.5 Hz), 127.6 (s), 127.3 (s), 127.2 (s), 126.3 (t, J_{C-P} = 11.5 Hz). ³¹P{¹H} NMR (202.16 MHz; CD₂Cl₂): δ 56.0 (J_{Pt-P} = 2635 Hz, d, 2P), 31.8 (s, 1P). Elemental analysis was obtained on a recrystallized sample. Calcd (%) for C₅₄H₄₂PtCl₂OP₃Sb·0.5(CHCl₃): C, 52.5; H, 3.44. Found: C, 52.26; H, 3.64. These results are consistent with the partial loss of the interstitial CHCl₃ molecules.

Synthesis of [2-CNCy][Cl]₂: Cyclohexyl isocyanide (50 μ L, 0.402 mmol) was added to a stirred solution of [2-Cl][Cl] (24.5 mg, 0.0206 mmol) in CH₂Cl₂ (2 mL). After stirring for 30 minutes, the solution was filtered through celite and evaporated to dryness. The residue was then dissolved in CH₂Cl₂ (2 mL) and precipitation was induced by addition of pentane (4 mL). Following recrystallization and successive washes with pentane (3 \times 5 mL), [2-CNCy][Cl]₂ was obtained as a crude product (30 mg, 0.0231 mmol). This compound could not be isolated in an analytically pure form. ¹H NMR (499.42 MHz; CDCl₃): 8.97 (d, J_{H-H} = 7.5 Hz, 2H, *o*-SbC₆H₄), 7.98 (brs, 4H), 7.62 (m, 2H), 7.49–7.58 (m, 6H), 7.42–7.49 (brs, 8H), 7.34–7.39 (brs, 6H), 7.27–7.34 (brs, 4H), 7.13–7.25 (brs, 6H), 7.05–7.13 (brs, 2H), 6.79 (brs, J_{H-H} = 7.8 Hz, 1H), 6.49 (brs, 1H), 3.73 (brs, 1H), 1.40–1.51 (brs, 2H), 1.28–1.39 (m, 1H), 1.13–1.28 (m, 5H), 1.07 (m, 2H). ¹³C{¹H} NMR (125.58 MHz; CDCl₃): 137.7 (brs), 135.1 (brs), 134.1 (brs), 133.6 (brs), 132.1 (d, J_{C-P} = 12 Hz), 129.5 (brs), 129.1 (brs), 128.6 (brs), 128.4 (brs), 55.6 (s, Cy-CH), 31.1 (s, Cy-CH₂), 24.4 (s, Cy-CH₂), 22.5 (s, Cy-CH₂). ³¹P{¹H} NMR (202.16 MHz; CD₂Cl₂): δ 45.5 (J_{Pt-P} = 2582 Hz, d, 2P), 30.8 ppm (s, 1P). IR (solid, attenuated total reflection measurement): ν_{NC} = 2229 cm⁻¹.

Synthesis of [2-CNCy][BF₄]₂: Cyclohexyl isocyanide (50 μ L, 0.402 mmol) was added to a stirred solution of [2-Cl][Cl] (50 mg, 0.042 mmol) and AgBF₄ (20.0 mg, 0.103 mmol) in CH₂Cl₂ (5 mL). After stirring for 30 minutes, the solution was filtered through celite and evaporated to dryness. The

residue was then dissolved in CH₂Cl₂ (3 mL) and precipitation was induced by addition of pentane (3 mL). The product was isolated by decantation and washed with pentane (2 \times 3 mL). This procedure afforded a 50% yield of [2-CNCy][BF₄]₂ (29.5 mg). Crystals suitable for X-ray diffraction were obtained by vapor diffusion of Et₂O into a solution of [2-CNCy][BF₄]₂ in CH₂Cl₂ at room temperature. ¹H (499.42 MHz; CD₂Cl₂): 8.97 (d, J_{H-H} = 6.9 Hz, 2H, *o*-SbC₆H₄), 7.63–7.70 (m, 3H), 7.53–7.62 (m, 14H), 7.45–7.52 (m, 4H), 7.33–7.45 (m, 10H), 7.23–7.34 (m, 7H), 7.2 (t, J_{H-H} = 6.9 Hz, 1H), 6.92 (d, J_{H-P} = 31.6 Hz, 1H), 3.7 (brs, 1H), 1.40–1.50 (brs, 2H), 1.28–1.39 (m, 1H), 1.13–1.28 (m, 5H), 1.07 (m, 2H). ¹³C{¹H} NMR (125.58 MHz; CD₂Cl₂): 142.2 (d, J_{C-P} = 35.6 Hz), 138.3 (d, J_{C-P} = 12 Hz), 137.9 (m), 137.5 (m), 134.1 (d, J_{C-P} = 2.9 Hz), 133.4 (m), 133 (d, J_{C-P} = 33.8 Hz), 132.7 (m), 132.1 (d, J_{C-P} = 12 Hz), 131.5 (d, J_{C-P} = 12 Hz), 129.9 (m), 129.1 (s), 127.6 (d, J_{C-P} = 108 Hz), 126.9 (s), 55.6 (s, Cy-CH), 31.3 (s, Cy-CH₂), 24.4 (s, Cy-CH₂), 22.5 (s, Cy-CH₂). ³¹P{¹H} NMR (202.16 MHz; CD₂Cl₂): δ 50.9 (J_{Pt-P} = 2477.6, d, 2P), 30.5 ppm (s, 1P). ¹⁹F{¹H} NMR (376.56 MHz; CD₂Cl₂): δ -153.28 ppm (s, ¹¹BF), -153.23 ppm (s, ¹⁰BF). IR (solid, attenuated total reflectance measurement): ν_{NC} = 2232 cm⁻¹. Elemental analysis. Calcd (%) for C₆₁H₅₃NPtOP₃SbB₂F₈: C, 52.32; H, 3.82. Found: C, 52.59; H, 3.81.

Procedure for the *in situ* generation of the dicationic complexes

1-Cl₂ or [2-Cl][Cl] was dissolved in CD₂Cl₂ (0.7 mL). The resulting solution was subsequently treated with phenylacetylene and AgBF₄. The sample was then subjected to ³¹P{¹H} NMR spectroscopy, leading to the spectra shown in Figure 3. The quantities used for each measurements are as follows: 1-Cl₂ (9 mg, 0.00768 mmol), phenylacetylene (16 mg, 0.155 mmol) and AgBF₄ (4 mg, 0.0205 mmol); [2-Cl][Cl] (15 mg, 0.0126 mmol), phenylacetylene (26 mg, 0.252 mmol) and AgBF₄ (5 mg, 0.0252 mmol). This experiment was repeated with [2-Cl][Cl] and tht as a ligand. The resulting spectra are shown in Figure S12. The quantities used for each measurements are as follows: [2-Cl][Cl] (15 mg, 0.0126 mmol), tetrahydrothiophene (22 mg, 0.250 mmol) and AgBF₄ (6 mg, 0.0308 mmol).

General Procedure for the Catalytic Cycloisomerization Reactions

The catalytic reactions were carried out under N₂. In a typical experiment, 2-allyl-2-(2-propynyl)malonate (**a**) (178 mg, 0.707 mmol) was mixed with [2-Cl][Cl] (1 mol %, 8.4 mg, 0.007 mmol) and AgBF₄ (2 mol %, 3 mg, 0.015 mmol) in CDCl₃ (2 mL). Conversion was measured using ¹H NMR spectroscopy based on the integration of the starting material and product resonances. Conversion is defined [product]/([product] + [starting material]).

ASSOCIATED CONTENT

Supporting Information

Additional experimental and computational details. Crystallographic data in cif format. Optimized structures in xyz format. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

Accession Codes

CCDC 2090478 and 2090479 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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Author Contributions

HY synthesized [2-Cl][Cl]. JES synthesized and characterized all other complexes. JES also carried out the calculations and catalysis experiments. FPG oversaw the study.

Notes

The authors declare no competing financial interest.

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TOC graphic:

