Stabilization of an Intramolecularly Coordinated Stannylidenium Cation

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Dedicated to Professor Klaus Jurkschat on the Occasion of His 60th Birthday

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Abstract. The treatment of trans-{[2,6-(Me₂NCH₂)₂C₆H₃]SnI}₂PtI₂ with Na(pyt) (pyt = 2-mercaptopyridine) yielded the unprecedented complex {{[2,6-(Me₂NCH₂)₂C₆H₃]Sn}Pt(μ -pyt)₂I} (1), where a Sn \leftarrow N coordinated stannylidenium (LSn^{II})⁺ fragment donates a to a

Introduction

The chemistry of transition metal (TM) complexes containing various Sn^{II}-based ligands is an active research area since they seem to be catalytic reagents for a variety of reactions, depending on the type of transition metal involved.^[1] Tin dichloride, as the simplest example of Sn^{II}-based ligands, is an important co-catalyst in various group 10 metal-catalyzed reactions such as hydroformylation,^[2] hydrogenation,^[3] isomerization,^[4] or hydrogen-mediated reductive couplings.^[5] These TM-Sn^{II} complexes are usually prepared by reactions of the TM-Cl complexes with stannylene SnR_2 (where R is an organic or inorganic substituent), via the insertion of a SnR_2 into a TM-Cl bond to yield complexes of the general formula [TM- SnR_2Cl having weakly coordinated $[SnR_2Cl]^-$ anions.^[6] This weak coordination of [SnR₂Cl]⁻ anion and/or its trans-labilizing effect has been used to explain the importance of stannylenes SnR_2 as co-catalysts. The exact role of the SnR_2 fragments is still unclear^[7] and studies dealing with the synthesis and properties of TM complexes that contain various Sn^{II}based ligands are of interest for this reason. Recently, Deelman et al. reported that the reaction of $SnCl_2$ with [M(X)(Cl)(2- $PyPPh_{2}$] precursors (X = Cl, Me) yielded cationic complexes $[M(X)(SnCl_2(2-PyPPh_2)_2)]^+$, in which a dichlorostannylene

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moiety is stabilized by intramolecular coordination of the pyridyl groups^[8] (Scheme 1A) and we have also reported the isolation of $[(\{2,6-(Me_2NCH_2)_2C_6H_3\}Sn)(\mu-pyt)_2PtCl]$, where 2mercaptopyridine was used as the bridge for a Sn^{II} cation and

a Pt^{II} anion (hereafter, pyt = 2-mercaptopyridine)

 $[Pt^{II}(pyt)_2I]^-$ anion. Compound 1 was characterized by NMR spec-

troscopy and molecular structure was determined by X-ray diffraction

analysis. The bonding situation in 1 was analyzed by DFT studies.



Scheme 1. Tin-platinum complexes stabilized by intramolecular coordination.

Herein, we present the synthesis of $[({2,6-(Me_2NCH_2)_2C_6H_3}Sn)(\mu-pyt)_2PtI]$ (1), an iodide analogue of the latter compound. Complex 1 was characterized by NMR spectroscopy, elemental analysis and the molecular structure was determined by single-crystal X-ray diffraction analysis. Furthermore, theoretical calculations using density functional theory (DFT) were performed on compound 1.

Results and Discussion

The reaction of *trans*- $\{[2,6-(Me_2NCH_2)_2C_6H_3]SnI\}_2PtI_2$ with 3 equiv. of Na(pyt) yielded the complexes $\{2,6-(Me_2NCH_2)_2C_6H_3\}Sn(pyt)$ and $[(\{2,6-(Me_2NCH_2)_2C_6H_3\}Sn)-(\mu-pyt)_2PtI]$ (1) (Scheme 2).

While the by-product $\{2,6-(Me_2NCH_2)_2C_6H_3\}$ Sn(pyt) was isolated and characterized according to previous NMR spectroscopic data,^[9] the sparingly soluble compound **1** represents a

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Scheme 2. Synthesis of complex 1.

new Sn^{II} \rightarrow Pt^{II} complex that was characterized by ¹H NMR spectroscopy and single-crystal X-ray diffraction analysis. The ¹H NMR spectrum revealed a singlet of the CH₂N protons at $\delta = 3.69$ ppm, a singlet of the NCH₃ protons at $\delta = 2.19$ ppm of the N,C,N-chelating ligand. The signals at 6.58, 6.75, 7.49, and 7.87 ppm confirmed the presence of the pyt polar group. Other NMR spectroscopic data could not be obtained due to the poor solubility of **1** in organic solvents. The molecular structure of compound **1** was, however, determined by singlecrystal X-ray diffraction analysis and is depicted in Figure 1. Selected geometrical parameters are given in the Figure caption.



Figure 1. Molecular structure of 1 together with selected bond lengths /Å and angles /°: The thermal ellipsoids are drawn with 50% probability. Hydrogen atoms and one CH_2Cl_2 molecule are omitted for clarity. Selected bond lengths /Å and angles /°: Sn(1)–Pt(1) 2.4712(5), Pt(1)–I(1) 2.6757(5), Pt(1)–S(1a) 2.2748(17), Pt(1)–S(1) 2.2748(17), Sn(1)–N(1) 2.437(5), Sn(1)–N(2) 2.414(4), Sn(1)–C(1) 2.127(8); Sn(1)–Pt(1)–I(1) 180.00, S(1)–Pt(1)–S(1a) 173.80(6), S(1)–Pt(1)–I(1) 86.90(3), Sn(1)–Pt(1)–S(1) 93.10(3).

The structure of **1** consists of a four-coordinate platinum atom with a square-planar configuration and a six-coordinate Sn^{II} atom with a distorted octahedral arrangement. Complex **1** exhibits a unique I–Pt^{II}–Sn^{II}–C bond bridged by two head-tohead coordinating pyt ligands. The closest structural analogy is the cationic square-planar platinum complex *trans*-[Pt(Me) (SnCl₂)(2-PyPPh₂)₂]⁺[BF₄]⁻ in which the Pt–SnCl₂ bond is bridged by two head-to-head coordinated 2-PyPPh₂ ligands^[8] and the neutral complex [PdSn(μ -mt)₄Cl₂] with the Pd^{II}→Sn^{IV} dative bond bridged by four methimazolyl (mt) groups.^[10]

The square planar configuration of the Pt(1) atom is formed by the S(1) and S(1a) atoms of the pyt groups, and by the Sn(1) and the I(1) atoms. The Sn(1) and I(1), and S(1) and S(1A) atoms are mutually *trans* with Sn(1)-Pt(1)-I(1) and S(1)-Pt(1)-S(1a) bond angles of 180.0° and $173.80(6)^{\circ}$. respectively. The distances of the Pt(1)-I(1) [2.6757(5)Å], Pt(1)-S(1) and Pt(1)-S(1a) [2.2748(17) Å] bonds correspond to covalent Pt-I and Pt-S bonds found in other Pt^{II} complexes containing pyridine-2-thionate ligands.^[11] The Sn(1)-Pt(1) bond length of 2.4712(5) Å in **1** is comparable to that found in $[(\{2,6-(Me_2NCH_2)_2C_6H_3\}Sn)(\mu-pyt)_2PtCl]$ [2.4661(6) Å],^[9] but is significantly shorter than that found in the cationic square-planar platinum complex trans-[Pt(Me)(SnCl₂)(2- $PyPPh_{2}^{2}^{+}[BF_{4}]^{-}$ [2.5166(6) Å].^[8] In relation to the theoretical single Sn-Pt bond estimated to 2.63 Å by Pyvkkö and Atsumi,^[12] the value of 2.4712(5) Å appears rather short. However, the comparison with the theoretical Sn-Pt double bond $(2.42 \text{ Å})^{[12]}$ reveals that the present Sn(1)-Pt(1) bond length is too long for a double bond. The octahedral coordination arrangement of the Sn(1) atom consists of two nitrogen atoms N(1), N(1a) of the ligand L, two nitrogen atoms N(2), N(2a)of pyt groups and the C(1) and Pt(1) atoms all being mutually in *trans* positions as defined from N(1)-Sn(1)-N(1a) = $150.12(2)^{\circ}$, N(2)-Sn(1)-N(2a) = 174.92(19)^{\circ}, and C(1)- $Sn(1)-Pt(1) = 180.0^{\circ}$. The most interesting feature is that the values of all Sn-N bond lengths [range of 2.414(4)-2.437(5) Å] indicate the presence of Sn←N donor-acceptor interactions, leaving thus the C(1)-Sn(1) bond [2.127(8) Å] as the only covalent bond of the central Sn^{II} atom. The latter fact together with the presence of three covalent bonds at Pt^{II} suggest the presence of a Sn←N coordinated stannylidenium $(LSn^{II})^{+}$ fragment donating to a $[Pt(pyt)_{2}I]^{-}$ anion. Apparently, an additional intramolecular donation of the nitrogen lone pairs of the pyt ligands to the tin atom, leading to a hexacoordinate octahedral arrangement, seems to stabilize the stannylideniumtype coordination of the (LSn^{II})⁺ moiety on the central Pt^{II} atom.

To gain theoretical insight into the bonding situation in 1, DFT calculations were performed. The geometry optimization using the BP86/def2-TZVP methodology reproduces the arrangement of the solid state very well. Use of fully relativistic effective core potentials yielded no significant difference in comparison to non-relativistic effective core potentials (see Supporting Information). The bonding situation can be interpreted as a Sn \leftarrow N coordinated stannylidenium (LSn^{II})⁺ fragment donating to a [Pt^{II}(pyt)₂Cl]⁻ anion. The Sn–Pt binding orbital is depicted at Figure 2.

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Figure 2. The Sn-Pt-binding orbital of complex 1.

The NBO analysis^[13] revealed no lone pair at the tin atom and the natural charge of tin atom is +1.715, while that at the platinum atom is -0.712. These observations can be rationalized with the lone electron pair of the Sn^{II} atom being shared by both atoms and consumed for the formation of a covalent tin-platinum bond. The NBO analysis^[13] showed that the nature of the Sn-Pt bond is mediated by sp-hybridized orbitals on the tin atom (one sp-hybrid for the Sn-Pt bond and one for the Sn-C bond). The natural electron configuration of the tin atom is $5s^{1.25}$ and $5p^{0.98}$ indicating that nearly one electron was fully consumed for the formation of this bond and suggests highly covalent character of this bond. The Wiberg bond index of this bond amounts to 0.762. However, the formal presence of two covalent bonds on the tin atom with the natural charge of about + 2 and the negative formal charge on platinum also suggests another possible interpretation of the Sn-Pt bond to be a Sn^{IV}←Pt⁰ interaction.^[10] This is in accordance with the larger electronegativity of platinum in comparison to tin. Hence, the electrons of the covalent Sn-Pt bond have to be counted for platinum. The nature of the Sn-Pt interaction can thus be described by both frontier formulae until further measurements (such as Mössbauer spectroscopy) clarify the tin oxidation state.

The highly positively charged tin atom (+ 1.715, and formally + IV with this interpretation) is further stabilized by several strong N donor interactions and an additional donor interaction (found with second order perturbation theory) of Pt \rightarrow Sn (Table 1), hence lowering the formal charge. This is in line with the shortened Sn–Pt bond length. Moreover, the ionic part of a Sn^{IV} \leftarrow Pt⁰ interaction supports the decrease of the Sn–Pt bond length. The sulfur–platinum bonds have covalent character (75% S, 25% Pt) but they are supported by additional donor interactions from the sulfur atoms. The whole system is strongly delocalized, which is reflected in the donor interactions from the lone pairs of the platinum atom into the C–Sn bond and the Pt–Sn bond (antibonding orbitals BD*).

Table 1. Second order perturbation analysis. a) BD: binding electron pair. b) LP: lone pair.

Charge Transfer	Energy /kcal·mol ⁻¹
$\overline{LP^{a)}(Pt) \rightarrow LP^{*}(Sn)}$	6.08
$LP(S) \rightarrow LP^*(Pt)$	15.94
$LP(I) \rightarrow LP^{*}(Pt)$	7.74
$LP(py) \rightarrow LP^*(Sn)$	75.03
$LP(amine) \rightarrow LP^*(Sn)$	46.88
$LP(py) \rightarrow LP^*(Sn)$	75.03
$LP(amine) \rightarrow LP^*(Sn)$	46.88
$LP(Pt) \rightarrow BD^{b)*}(Sn-C)$	10.05
$LP(Pt) \rightarrow BD^{*}(Pt-Sn)$	6.73
$BD(Sn-C) \rightarrow BD^*(Sn-Pt)$	15.47

Conclusions

The treatment of *trans*-{[2,6-(Me₂NCH₂)₂C₆H₃]SnI}₂PtI₂ with Na(pyt) yielded the unprecedented complex [({2,6-(Me₂NCH₂)₂C₆H₃}Sn)(μ -pyt)₂PtI] (1), where a Sn \leftarrow N coordinated stannylidenium (LSn^{II})⁺ fragment donates to a [Pt^{II}(pyt)₂-Cl]⁻ anion. The bonding situation in 1 was analyzed by DFT and showed that the nature of the Sn–Pt interaction is very complex. The lone electron pair of Sn^{II} atom was consumed for the formation of the tin–platinum bond and Sn^{II} \rightarrow Pt^{II} donation in this complex can be also interpreted as a Sn^{IV} \leftarrow Pt⁰ interaction.

Experimental Section

General: All reactions were carried out in an argon atmosphere, using standard Schlenk techniques. Solvents were dried by standard methods, distilled prior to use. The starting compound *trans*-{[2,6-(Me₂NCH₂)₂-C₆H₃]SnI}₂PtI₂ was prepared according to the literature^[14] and NaI and H(pyt) was purchased from Sigma-Aldrich. The ¹H NMR spectra were recorded at ambient temperature with a Bruker Avance 500 spectrometer. The chemical shifts δ are given in ppm and referenced to external SiMe₄ (¹H).

Synthesis of $[{(2,6-(Me_2NCH_2)_2C_6H_3)Sn}Pt(\mu-pyt)_2I]$ (1): A solution of trans-{[2,6-(Me₂NCH₂)₂C₆H₃]SnI}₂PtI₂ (0.18 g, 0.14 mmol) in CH₂Cl₂ (40 mL) was stirred with Na(pyt) (0.57 g, 0.42 mmol) in THF (40 mL) for 24 h. The resulting mixture was filtered, evaporated to dryness, and the solid residue was extracted with toluene $(2 \times 5 \text{ mL})$. The toluene fraction was evaporated and the solid residue characterized as {2,6-(Me₂NCH₂)₂C₆H₃}Sn(pyt) by NMR spectroscopic data, which were consistent with those published previously.^[9] The solid residue insoluble in toluene was extracted with CH_2Cl_2 (2×15 mL) and organic solution was concentrated by slow evaporation of CH₂Cl₂ to approx. 5 mL during of what the crystalline material suitable for Xray structure analysis appeared. The crystalline material was separated by decantation and washed with hexane to give complex 1 as red solid. Yield 48 mg (40%); m.p. 245 °C (decomp.). C₂₂H₂₉IN₄PtS₂Sn (854.32): calcd. C 30.93; H 3.42%; found: C 30.90; H 3.39%. ¹H **NMR** (500.13 MHz, CDCl₃): δ = 7.87 (d, 2 H, pyridine), 7.49 (t, 2 H, pyridine), 7.20 (d, 2 H, ArH), 7.03 (t, 1 H, ArH), 6.75 (d, 2 H, pyridine), 6.58 (t, 2 H, pyridine), 3.69 (s, 4 H, CH₂N), 2.19 (s, 12 H, NCH₃) ppm.

Crystallographic Details for Compound 1: Single crystals of **1** (orange) were obtained by slow evaporation from their respective solutions in dichloromethane. Compound **1** crystallized as a solvate with

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CH₂Cl₂ molecule. Crystals were mounted on a glass fiber with epoxy cement and measured with a KappaCCD diffractometer with a CCD area detector by monochromatized Mo- K_{α} radiation ($\lambda = 0.71073$ Å) at 150(1) K. The details pertaining to the data collection and refinement follows for crystals are as for 1-CH₂Cl₂: C₂₁H₂₇IN₄PtS₂Sn•CH₂Cl₂, M.w. = 925.19, monoclinic, space group C2/c, a = 14.3761(8), b = 14.1379(9), c = 17.0359(11) Å, $a = 90^{\circ}$, $\beta =$ $108.837(9)^{\circ}$, $\gamma = 90^{\circ}$, Z = 4, ρ (calcd) = 1.875 Mg·m⁻³, $\mu = 6.275$ mm⁻¹, crystal size $0.39 \times 0.31 \times 0.09$ mm, crystal shape plate, θ range 1 to 25.75°, 17847 reflections collected, of which 3706 were independent $[R(int) = 0.046], [I > 2\sigma(I)]: R_1 = 0.0394, wR_2 = 0.0982.$

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-795541 (Fax: +44-1223-336-033; E-Mail: deposit@-ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

Supporting Information (see footnote on the first page of this article): Crystallographic details, CIF. file and computational details.

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