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Synthesis and Reactivity of a Platinum(II) Complex with Hydrosulfido Ligands Induced by a Chelated *N*-Heterocyclic Carbene Ligand

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A bis(hydrosulfido)platinum(II) complex with a bidentate chelate *N*-heterocyclic carbene ligand was oxidized by O_2 to give a linear tetrasulfide complex in the presence of excess hydrogen sulfide and a thiosulfato-bridged dinuclear complex without hydrogen sulfide.

Sulfur-containing metal complexes are important in the formation of ores, some biological reactions, industrial processes, such as hydrodesulfurization, and nature's sulfur cycle.[1] Because sulfur atoms can adopt a wide range of oxidation states between −2 and +6, metal–S complexes show rich chemistry, including redox reactions and C–S bond formations. For example, a trinuclear complex $[(\mathrm{IrCp}^*)_3(\mu\text{-S})_2]^{2+}$ (Cp*: η^5-1,2,3,4,5-pentamethylcyclopentadienyl) catalyzes the electrochemical reduction of carbon dioxide to give oxalate.[2] However, the reactions of metal complexes involving sulfur atoms can be complicated due to the wide range of the oxidation states and bridging abilities of sulfur atoms. In order to investigate the reactivity of S ligands, ancillary ligands, such as phosphines[3] and cyclopentadienyl derivatives,[2,4] are often needed to avoid the formation of vacant coordination sites on the metal ions, thus preventing reactions involving both the metal ion and S atom.

N-Heterocyclic carbene (NHC) ligands are phosphine alternatives and strong σ-donors, which increase the electron density on metal ions and have been used for catalysts in organic reactions.[5] NHCs can be good candidates for ancillary ligands to investigate reactions of metal–SH and metal–S complexes due to the increased electron density on the metal ions, which causes the S atoms to become more reactive. To date, only a series of the hydrosulfido NHC ruthenium complexes, $[\mathrm{Ru(IMes)_2(CO)(SH)_2}]$, *all-trans*-$[\mathrm{Ru(IMes)_2(CO)_2(SH)_2}]$, and *tcc*-$[\mathrm{Ru(IMes)_2(CO)_2(SH)H}]$,[6] have been reported.

To investigate the reactivity of sulfur atoms on an NHC metal unit, we synthesized a bis(hydrosulfido)platinum(II) complex with a bidentate chelate NHC ligand, *cis*-$[\mathrm{Pt(bisNHC)(SH)_2}]$ (**1**) (bisNHC: 1,1′-dimethyl-3,3′-ethylene-4-diimidazolyldiylidene), by the reaction of *cis*-$[\mathrm{Pt(bisNHC)(OAc)_2}]$ and hydrogen sulfide in acetonitrile. To the best of our knowledge, **1** is the first example of an NHC hydrosulfido platinum complex. We believed that it would be possible to prepare S-containing multinuclear complexes similar to corresponding phosphine complexes.[3]

Although no SH protons were found in the X-ray crystallographic analysis of **1** (Figure 1), in ^{1}H NMR spectra of **1** in $\mathrm{CDCl_3}$, a signal for the SH protons with ^{195}Pt satellites ($^2J_{\mathrm{Pt-H}} = 51.2$ Hz) was observed at −1.18 ppm and ν_{SH} appeared at 2540 cm^{-1}. The two methylene units of the ethylene bridge in the bisNHC ligand were inequivalent in the crystal structure, whereas they are equivalent in solution and showed two AA′BB′ signals in the ^{1}H NMR spectrum. This result suggests that the free rotation of the Pt–C bonds is prohibited and that a smaller conformational change of the chelate ring is allowed.

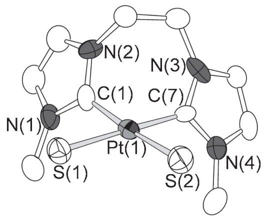


Figure 1. ORTEP drawing of **1** with 50% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pt(1)–S(1) 2.372(5), Pt(1)–S(2) 2.354(5), Pt(1)–C(1) 2.005(16), Pt(1)–C(7) 2.021(14), S(1)–Pt(1)–S(2) 88.53(17), S(1)–Pt(1)–C(1) 92.6(4), S(2)–Pt(1)–C(7) 94.9(4), C(1)–Pt(1)–C(7) 84.3(6), S(1)–Pt(1)–C(7) 175.2(4), S(2)–Pt(1)–C(1) 175.1(4).

Complex **1** was stable in chloroform but was slowly oxidized in methanol or acetonitrile by O_2 in the presence of excess hydrogen sulfide to afford quantitatively the terminally coordinated linear tetrasulfido complex, *cis*-$[\mathrm{Pt(bisNHC)(S_4)}]$ (**2**) (Figure 2). Similar tetrasulfido complexes with phosphine ancillary ligands have been obtained by the reactions of precursors other than hydrosulfido complexes with elemental sulfur.[7] Although some bis(hydrosulfido) phosphine platinum complexes have been reported,[8] no reactions affording tetrasulfido complexes have been described. Oxidation of hydrosulfido ligands of iridium Cp* complexes with terminal or bridging hydrosulfido ligands, $[(\mathrm{IrCp^*Cl})_2(\mu\text{-SH})_2]$ and $[\mathrm{IrCp^*(PMe_3)(SH)_2}]$, by elemental sulfur or sulfur dioxide is reported to give the tetrasulfido complexes, $[\mathrm{IrCp^*}(\mu\text{-S_4})]_2$ and $[\mathrm{IrCp^*(PMe_3)(S_4)}]$, respectively.[9]

Complex **1** was reacted with O_2 in methanol in the absence of hydrogen sulfide to give a mixture of **2** and mainly two other side products confirmed by ^{1}H NMR spectroscopy (See Figure S3 in Supporting Information[18]). After slow evaporation of the solvent of the solution giving crystals of **2**, which were removed by filtration, a thiosulfate-bridged dinuclear complex,

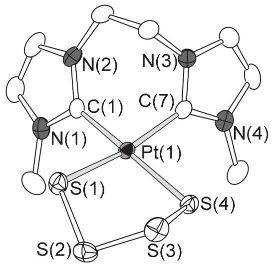


Figure 2. ORTEP drawing of **2** with 50% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pt(1)–S(1) 2.3500(14), Pt(1)–S(4) 2.3453(11), Pt(1)–C(1) 2.016(4), Pt(1)–C(7) 1.996(5), S(1)–S(2) 2.0709(15), S(2)–S(3) 2.0411(14), S(3)–S(4) 2.0643(18), S(1)–Pt(1)–S(4) 94.70(4), S(1)–Pt(1)–C(1) 90.58(12), S(4)–Pt(1)–C(7) 88.64(9), C(1)–Pt(1)–C(7) 87.66(14), S(1)–Pt(1)–C(7) 167.79(11), S(4)–Pt(1)–C(1) 171.14(12).

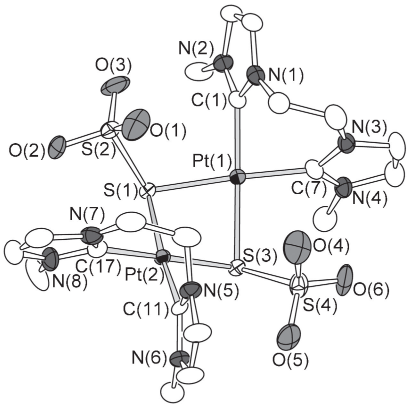
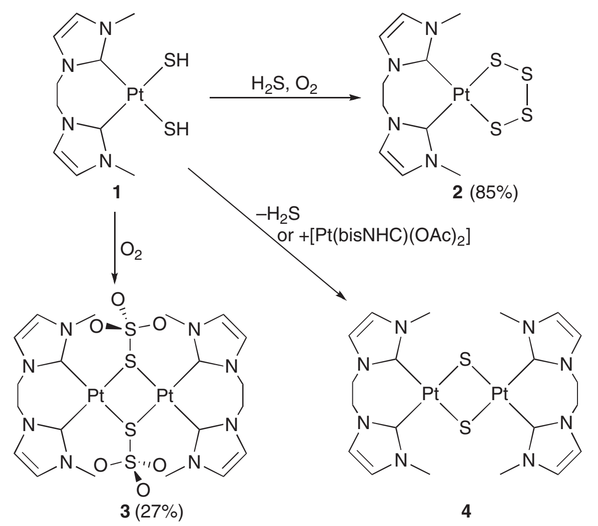


Figure 3. ORTEP drawing of **3** with 50% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pt(1)–S(1) 2.3605(16), Pt(1)–S(3) 2.358(2), Pt(2)–S(1) 2.3607(17), Pt(2)–S(3) 2.3555(14), Pt(1)–C(1) 1.991(8), Pt(1)–C(7) 1.987(7), Pt(2)–C(11) 1.985(7), Pt(2)–C(17) 1.986(6), S(1)–S(2) 2.127(2), S(3)–S(4) 2.129(2), S(2)–O(1) 1.434(6), S(2)–O(2) 1.447(6), S(2)–O(3) 1.433(8), S(4)–O(4) 1.438(6), S(4)–O(5) 1.442(8), S(4)–O(6) 1.444(6), S(1)–Pt(1)–S(3) 80.82(6), S(1)–Pt(2)–S(3) 80.87(6), S(1)–Pt(1)–C(1) 98.50(17), S(3)–Pt(1)–C(7) 96.5(3), S(1)–Pt(2)–C(17) 97.9(3), S(3)–Pt(2)–C(11) 98.17(16), C(1)–Pt(1)–C(7) 84.7(3), C(11)–Pt(2)–C(17) 83.2(3), S(1)–Pt(1)–C(7) 175.62(19), S(3)–Pt(1)–C(1) 172.00(17), S(1)–Pt(2)–C(11) 173.8(3), S(3)–Pt(2)–C(17) 177.78(19).



Scheme 1. Reactions of bis(hydrosulfide) NHC complex **1** to give tetrasulfide complex **2**, thiosulfate complex **3**, and bissulfido-bridged dinuclear complex **4**.

[{Pt(bisNHC)}$_2$(μ-SSO$_3$)$_2$] (**3**) was isolated from the filtrate (Figure 3). The Pt$_2$S$_2$ framework adopts a butterfly shape with a dihedral angle between the two coordination planes of the platinum ions of 127.59(13)°.

Many examples of thiosulfato complexes have been reported, and most of them have been prepared by reacting a precursor with sodium thiosulfate.[10] On the other hand, several thiosulfato platinum,[11] molybdenum,[12] chromium,[13] and ruthenium[14] complexes have been obtained by oxidizing disulfido or sulfido complexes with relatively strong oxidizing agents, such as SO$_2$, SO$_3$, PySO$_3$, or *t*-BuOOH. A few examples involving air oxidation affording thiosulfato complexes have been reported.[12,13] We believe that this difference in reactivity is due to the larger amount of electron density on the S atoms in the NHC complex than those in the analogous phosphine complexes.

The other side product of the oxidation reaction by O$_2$ without hydrogen sulfide showed the same ^{1}H NMR signals as those of the product obtained by the reaction of **1** with an equimolar amount of the acetato complex. This reaction of **1** and the acetato complex quantitatively gave one product, which can be a bissulfido-bridged dinuclear complex, [{Pt(bisNHC)}$_2$(μ-S)$_2$] (**4**). Isolation and structure analysis of **4** are in progress.

Scheme 1 shows summary of the reactions of hydrosulfido complex **1** to tetrasulfido complex **2**, thiosulfato complex **3**, and bissulfido-bridged dinuclear complex **4**.

Dinuclear[15] sulfido-bridged and mononuclear disulfido[11,16] platinum complexes with phosphine ligands have been reported. However, only dinuclear thiosulfate-bridged platinum complexes with amine or chelating thiosulfato ligands have been studied,[17] and no such complexes with phosphine ligands have been reported to our knowledge. The formation of **3** is the first example of oxidation of hydrosulfido or sulfido ligands with O$_2$ to thiosulfato ligands in a platinum complex, and the high reactivity toward oxidation or oxygenation of the sulfur ligands in the complexes was attributed to the σ-donating ability of the NHC ligands. Isolation of the bridging bis(sulfido) dinuclear complex and the preparation of multinuclear complexes are currently in progress.

In conclusion, the first bis(hydrosulfido)platinum complex having NHC ligands was synthesized. Introduction of NHC ligands caused changes in the reactivity of the sulfur ligands in comparison with those in the corresponding phosphine complexes. The ligands were oxidized affording a tetrasulfide complex in the presence of excess hydrogen sulfide and a thiosulfate-bridged dinuclear complex in air.

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18 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.