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C–S Bond Cleavage of Pyridine-2-thiol: A New Functionality of Quadruply Bridged Dinuclear Platinum and Palladium Complexes

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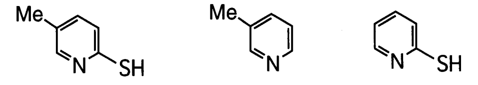
Treatment of pyridine-2-thiol (pytH) with H_2 (60 atm) in the presence of 5-methylpyridine-2-thiolate (5-mpyt)-bridged dinuclear Pt(III), Pt(II), or Pd(II) complexes (1 mol %) in DMF at 150 °C for 72 h leads to the formation of pyridine in 3–51% yield. From the ^1H NMR study of the exchange reactions and of the products under D_2 pressure, it is suggested that the catalytic reaction involves bimetallic activation of the pyt ligand followed by the liberation of pyridine and H_2S.

The limitation of the number of polynuclear metal complexes in unusual oxidation states hinders the studies on the reactivity and functionality of such complexes. The quadruply or doubly bridged dinuclear platinum and palladium complexes give an opportunity to study them, because it is easy to access the trivalent oxidation states.[1−3] The trivalent oxidation state in the dinuclear platinum and palladium complexes is stabilized by forming metal−metal bonding, and the facile redox between divalent and trivalent oxidation states can proceed without changing the bridging structure of the dinuclear unit. Thus, such Pt(II/III) and Pd(II/III) dimer systems may show reactivity and functionality characteristic of the facile redox reactions. For example, amidate-bridged dinuclear Pt(III) complexes catalyze ketonation and epoxidation of olefins.[4] 5-Methylpyridine-2-thiolate (5-mpyt)-bridged dinuclear platinum(III) complex $[Pt_2Cl_2(5\text{-mpyt})_4]$ reacts with tetrathiotungstate (WS_4^{2-}) in chloroform to give a tetrasulfide-bridged tetranuclear Pt(III) complex, $[\{ClPt_2(5\text{-mpyt})_4\}_2S_4]$.[5] In the course of our extended study on the reactivity of $[Pt_2Cl_2(5\text{-mpyt})_4]$, we found the liberation of 3-picoline formed by the C−S bond cleavage of the bridging ligand, 5-mpyt, in the reaction of $[Pt_2Cl_2(5\text{-mpyt})_4]$ with H_2. Because it indicates that the vacant site generated by the loss of the bridging ligands may be used for catalytic C−S bond cleavage, we examined the activity of 5-mpyt-bridged dinuclear Pt(III) complexes, as well as Pt(II) and Pd(II) complexes, toward the C−S bond cleavage of pyridine-2-thiol (pytH) as a substrate (Chart 1). We wish to report herein, for the first time, the catalytic hydrodesulfurization of pyridine-2-thiol by quadruply bridged dinuclear platinum and palladium complexes. The C−S bond cleavage of bridging pyridine-2-thiolate has been observed in the reaction of $[Re_2(pyt)_2(CO)_6]$ with $[Ru_3(CO)_{12}]$ in refluxing *m*-xylene under N_2, in which 2-pyridyl-bridged (Ru/Re)$_4$ mixed-metal complexes formed.[6] Homogeneous hydrodesulfurization reactions by metal complexes have also been reported.[7−10]

Chart 1



5-methylpyridine-2-thiol (5-mpytH)

3-picoline

pyridine-2-thiol (pytH)

When $[Pt_2Cl_2(5\text{-mpyt})_4]$ (**1**, Chart 2) was reacted with H_2 in DMF at 150 °C, the Pt(III) dimer liberated 3-picoline which was generated by the C−S bond cleavage of the bridging 5-mpyt ligand. The amount of 3-picoline increased with an increase of the hydrogen pressure and also depended on the reaction time. It finally reached about two molecules per dimer complex after 72 h under 60 atm of H_2.

Although the catalytic C−S bond cleavage of pyridine-2-thiol (pytH) does not occur in the presence of **1** as a catalyst

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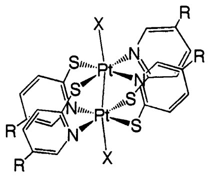
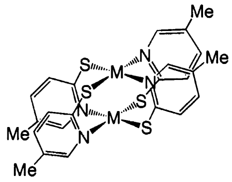
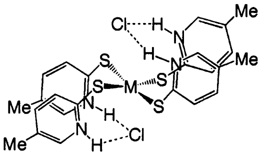
Chart 2



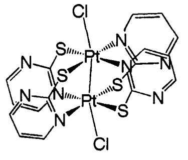
$[Pt_2X_2(R\text{-}pyt)_4]$ (R = Me, X = Cl, **1**; X = Br, **2**; X = I, **3**; R = H, X = Cl, **6**)



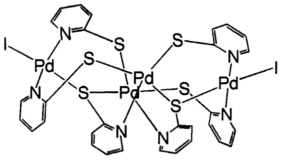
$[M_2(5\text{-}mpyt)_4]$ (M = Pt, **4**; M = Pd, **8**)



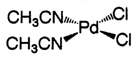
$[Pt(5\text{-}mpytH)_4]Cl_2$ (**5**)



$[Pt_2Cl_2(pymS)_4]$ (**7**)



$[Pd_4I_2(pyt)_6]$ (**9**)



$[PdCl_2(CH_3CN)_2]$ (**10**)

Table 1. Hydrogenolysis of Pyridine-2-thiol Catalyzed by Dinuclear Pt(III), Pt(II), and Pd(II) Complexes and Related Complexes[a]

catalyst	amount of pyridine (mmol)	TON[b]
$[Pt_2Cl_2(5\text{-}mpyt)_4]$ (**1**)	0.148	9.9
$[Pt_2Br_2(5\text{-}mpyt)_4]$ (**2**)	0.076	5.0
$[Pt_2I_2(5\text{-}mpyt)_4]$ (**3**)	0.044	2.9
$[Pt_2(5\text{-}mpyt)_4]$ (**4**)	0.113	7.5
$[Pt(5\text{-}mpytH)_4]Cl_2$ (**5**)	0.043	2.9
$[Pt_2Cl_2(pyt)_4]$ (**6**)	0.101	6.8
$[Pt_2Cl_2(pymS)_4]$ (**7**)	0.051	3.4
$[Pd_2(5\text{-}mpyt)_4]$ (**8**)	0.783	51
$[Pd_4I_2(pyt)_6]$ (**9**)	0.706	47
$[PdCl_2(CH_3CN)_2]$ (**10**)	0.445	29

[a] Reaction conditions: catalyst, 0.015 mmol; pyridine-2-thiol, 1.50 mmol; solvent, *N,N*-dimethylformamide (DMF), 3 mL; H_2 pressure, 60 atm; temperature, 150 °C; time, 72 h. [b] Turnover number = [product]/[complex].

under 1 atm of H_2 in DMF at 150 °C, it does proceed to generate pyridine with the H_2 pressure over 5 atm. The amount of the formed pyridine increased with an increase of the H_2 pressure.[11] However, no C−S bond cleavage was observed when PhSH was used as a substrate. The catalytic activities of **1** and related complexes are summarized in Table 1. Among the chloro dinuclear Pt(III) complexes (**1**, **6**, **7**), 5-mpyt-bridged complex **1** has the highest activity. It indicates that the catalytic activity is affected by the substituent group on the pyridine ring or by the heteroatom in it. A methyl group at the 5-position on the pyridine ring enhances the activity. The relatively inert dimer core of **7** toward the exchange reaction of bridging ligands also accounts for the low activity of **7**. It is noted that no C−S bond cleavage of the bridging ligand was detected even in the reaction of **7** with 60 atm of H_2 in the absence of the substrate in DMF at 150 °C. The details of the structure and redox properties of **7** are described elsewhere.[12]

General starting materials for Pt(II) complexes such as $K_2[PtCl_4]$ and $[PtCl_2(NH_3)_2]$ give mononuclear complex $[Pt(pytH)_4]Cl_2$ having a similar structure to **5** and dinuclear Pt(II) complex $[Pt_2(pyt)_4]$, respectively, in organic solvent in the presence of an excess amount of pytH.[13,14] The catalytic activity of the complex having 5-mpyt ligand is higher than that of the complex having pyt ligand. Thus, it is interesting to compare the activities of the dinuclear Pt(III) and Pt(II) and mononuclear Pt(II) complexes of 5-mpyt. As is obvious from Table 1, the activity of mononuclear complex **5** is lower than those of the dinuclear complexes. The activity of Pt(III) dimer **1** is slightly higher than that of Pt(II) dimer **4**. Accordingly, the presence of a Pt−Pt bond is more efficient for the catalytic C−S bond cleavage of the pyt ligand.

The nature of the axial ligands (X) in Pt(III) complexes $[Pt_2X_2(5\text{-}mpyt)_4]$ (X = Cl (**1**), X = Br (**2**), X = I (**3**)) also affects the activity. The activity decreases in the order X = Cl > Br > I, corresponding to the lability of the bridging ligands. The ^1H NMR spectra of **1**, **2**, and **3** in the presence of 2 equiv of pytH in $CDCl_3$ show the signal of free 5-mpytH, which resulted from the exchange of bridging 5-mpyt with added pytH. The facile exchange of 5-mpyt enhances the catalytic activity, the order also being X = Cl > Br > I.[15] It implies that the substitution of the axial ligand, X, by the substrate pytH takes place first (the substrate coordinates at the axial position through S donor atom), then it is followed by the exchange of the bridging 5-mpyt ligand for pyt ligand at the axial position, and finally, the C−S bond of the bridging pyt ligand is activated (Scheme 1).

It is interesting to note that the catalytic activities of the dinuclear and tetranuclear Pd(II) complexes **8** and **9** were found to be much higher than those of Pt complexes **1**−**7**. These Pd(II) complexes have bridging 5-mpyt or pyt ligands.[16] The activity of mononuclear complex $[PdCl_2(CH_3CN)_2]$ (**10**) is substantially lower than those of the dinuclear Pd(II) complexes. Mononuclear complex **10** forms $[Pd(pytH)_4]Cl_2$ in organic solvent similarly to the case of $K_2[PtCl_4]$. Thus, it is also evident here that the bimetallic activation of pyt ligand is the main path of the C−S bond cleavage as mentioned previously. The higher lability of Pd

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(11) Catalytic activity of **1** in DMF at 150 °C under various H_2 pressure (H_2 pressure, TON (turnover number = [product]/[complex])): 1 atm, 0; 10 atm, 2.9; 30 atm, 4.8; 60 atm, 9.9.

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(15) The amount of the exchanged 5-mpyt ligand was estimated by the intensity ratio of the methyl signal of the free and bridging 5-mpyt ligands: X = Cl, 16%; X = Br, 13%; X = I, 8%.

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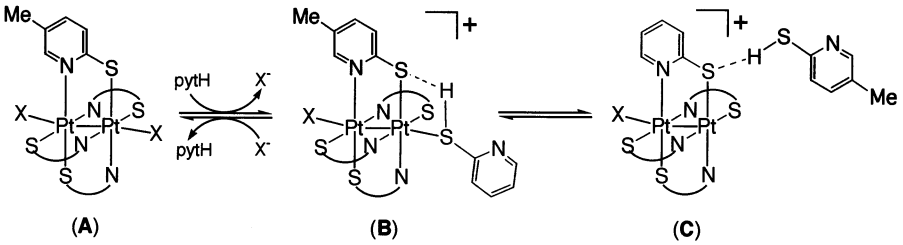
Scheme 1



complexes compared with Pt complexes accounts for the higher activity. Because the pyridinethiolato-bridged Pd(III) dimer[1] is unstable in solution at higher temperature, we could not compare the activity of the Pd(II) dimer with that of the Pd(III) dimer.

To elucidate the mechanism of the C−S bond cleavage, the reaction was conducted under D_2 atmosphere (8.5 atm) by using **1** as catalyst.[17] The volatile species formed by the reaction under D_2 as well as H_2 were trapped by distillation of the reaction mixture under reduced pressure. The ^{1}H NMR spectra of the volatile species are shown in Figure 1. From the reaction under H_2, the signals of pyridine formed by the C−S bond cleavage of pytH and those of 3-picoline formed from bridging 5-mpyt ligands were observed (Figure 1 (bottom)). The spectrum implies that the C−S bond cleavage of the bridging 5-mpyt proceeds when the reacting solution contains only a comparable amount of substrate to the catalyst. This is in contrast with the case of a catalytic reaction in the presence of the excess amount of pytH, because 3-picoline is not detected by gas chromatography. When the reaction was conducted under D_2 atmosphere, the intensities of the ortho proton of formed pyridine became half, and the H_6 signal of 3-picoline almost disappeared with changing the coupling pattern of the H_5 signal (Figure 1 (top)). These facts indicate that the deuteration occurred at the carbon atom bearing the C−S bond before hydrogenolysis. It is obvious now that the C−S bond cleavage reaction of pytH is the hydrogenolysis, and all of the introduced H atom or D atom came from H_2 or D_2 gas (Scheme 2). Because H_2S gas has been detected in the catalytic reactions under H_2, the reaction may involve the oxidative addition of H_2 to the species (C) in Scheme 1, successive C−S insertion, and the reductive elimination of pyridine and H_2S.

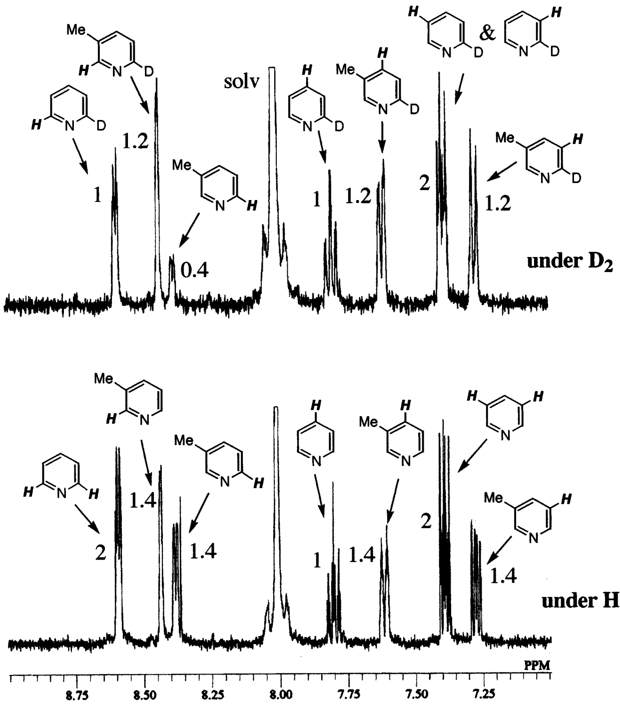
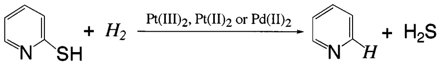


Figure 1. ^{1}H NMR spectra of the products formed by the hydrogenolysis of pyridine-2-thiol (pytH) in the presence of **1** under D_2 (top) and H_2 (bottom) in DMF-d_7.

Scheme 2



In summary, the catalytic activities of pyridinethiolate-bridged dinuclear Pt(III), Pt(II), and Pd(II) complexes toward C−S bond cleavage of pytH have been studied. The reaction proceeds via bimetallic activation of pyt ligand followed by the liberation of pyridine and H_2S. Pd(II) dimer **8** has the highest activity.

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(17) Reaction conditions: catalyst, **1**, 0.015 mmol; pytH, 0.030 mmol; solvent, DMF-d_7, 3 mL; D_2, 8.5 atm; temperature, 150 °C; time, 72 h. No substrate pytH was detected in the reaction mixture by gas chromatography.