

# Rearrangement of a (Dithiolato)Pt<sup>II</sup> Complex Formed by Reaction of a Cyclic Disulfide, 5,6-Dithiabicyclo[4.2.1]nona-1,3-diene, with a Platinum(0) Complex. Oxidation of the Rearranged (Dithiolato)Pt<sup>II</sup> Complex

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**Abstract:** The reaction of the title bicyclic disulfide (**16**) with (Ph<sub>3</sub>P)<sub>2</sub>Pt(η<sup>2</sup>-C<sub>2</sub>H<sub>4</sub>) (**2**) yielded the corresponding (dithiolato)Pt<sup>II</sup> complex (**17**) by oxidative addition. The initial product **17** isomerized at room temperature in a manner of [1,5]-sulfur rearrangement to give another (dithiolato)Pt<sup>II</sup> complex **18** in high

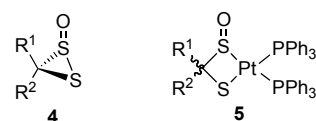
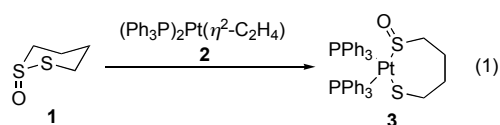
isolated yield. Oxidation reactions of **18** with dimethyldioxirane (DMD) provided (sulfenato-thiolato)- (**23**), (sulfinato-thiolato)- (**24**), (sulfinato-sulfinato)- (**25**), and (disulfinato)Pt<sup>II</sup> (**26**) complexes, the structures of which were elucidated by NMR spectroscopies and X-ray crystallography. The oxidation took

place regioselectively in the first step and chemoselectively in the second step. The selectivities are discussed.

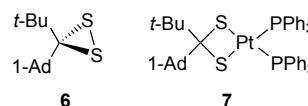
**Keywords:** disulfide • DFT calculations • oxidation • oxidative addition • platinum complex • rearrangement • X-ray crystallography

## Introduction

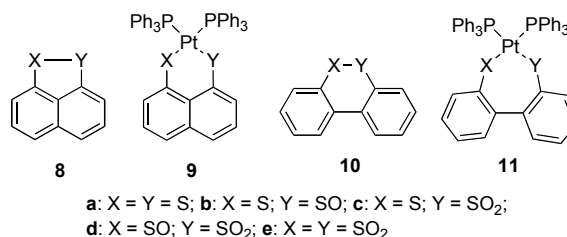
The oxidative addition of a sulfur-sulfur bond in cyclic sulfur compounds toward platinum(0) complexes is a topic of recent research activity.<sup>[1–11]</sup> Weigand and coworkers reported that the reaction of dithiane 1-oxide **1** with (Ph<sub>3</sub>P)<sub>2</sub>Pt(η<sup>2</sup>-C<sub>2</sub>H<sub>4</sub>) (**2**) gave (sulfenato-thiolato)Pt<sup>II</sup> complex **3** in high yield (Eq. 1).<sup>[2–7]</sup> This reaction was applied to three-membered cyclic thiosulfonates, dithiirane 1-oxides **4**, and the reaction of **4** with **2** yielded the corresponding four-membered (sulfenato-thiolato)Pt<sup>II</sup> complexes **5** in high yields.<sup>[8,9]</sup> We also found the reaction of dithiirane **6** with **2** provided (dithiolato)Pt<sup>II</sup> complex **7**.<sup>[10]</sup>



**a:** R<sup>1</sup> = R<sup>2</sup> = 1-adamantyl (1-Ad);  
**b:** R<sup>1</sup> = *t*-Bu, R<sup>2</sup> = 1-Ad; **c:** R<sup>1</sup> = 1-Ad, R<sup>2</sup> = *t*-Bu;  
**d:** R<sup>1</sup> = Ph, R<sup>2</sup> = 1-Ad; **e:** R<sup>1</sup> = H, R<sup>2</sup> = 9-triptycyl



Woollins and coworkers examined the reactions of **8a** and its oxides **8b–e** with Pt(PPh<sub>3</sub>)<sub>4</sub> to obtain the corresponding Pt<sup>II</sup> complex **9a** and its monoxide to tetraoxide **9b–e**, respectively, which were characterized by X-ray crystallography and NMR spectroscopies, in particular <sup>31</sup>P NMR.<sup>[11]</sup> They also reported the reaction of **10a–d** with Pt(PPh<sub>3</sub>)<sub>4</sub> giving rise to the corresponding **11**.<sup>[12]</sup>



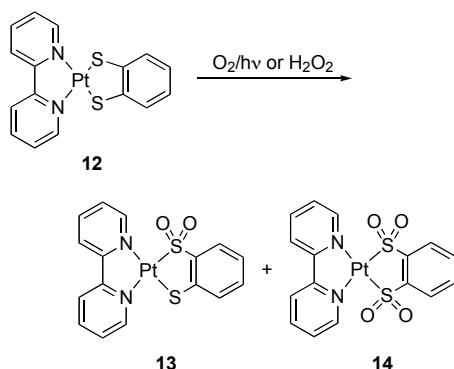
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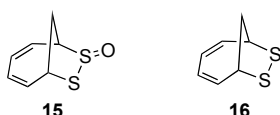
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S-Oxides of (dithiolato)Pt<sup>II</sup> complexes can also be prepared by their oxidation.<sup>[13–15]</sup> Photooxidation of (diimino-dithiolato)Pt<sup>II</sup> complex **12** with molecular oxygen yielded (sulfinato-thiolato)Pt<sup>II</sup>

**13** and (disulfinato)Pt<sup>II</sup> complexes **14**,<sup>[14]</sup> and the oxidation of **13** with H<sub>2</sub>O<sub>2</sub> (excess) gave **14**.<sup>[15]</sup> However, the oxidation reaction of (dithiolato)Pt<sup>II</sup> complexes has been barely investigated so far, compared with those of (dithiolato)M<sup>II</sup> complexes (M = Ni and Pd) of the same Group X elements that have been investigated in detail<sup>[16-27]</sup> in relation to the air sensitivity of transition metal thiolates.<sup>[16]</sup>

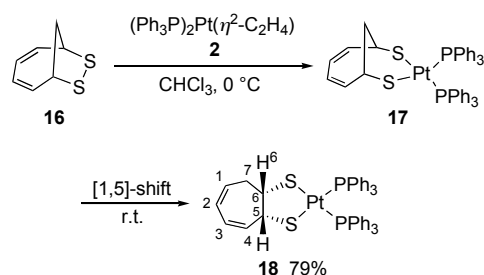


Recently we reported that the reaction of cycloheptatriene with S<sub>8</sub>O gave bicyclic thiosulfate **15**.<sup>[28]</sup> Compound **15** was reduced with Lawesson's reagent to give bicyclic disulfide **16** as an orange oil, which was unstable to polymerize within a few hours. The instability of **16** is ascribed to the large strain of the disulfide bond. The calculated S-S bond length and the C-S-S-C dihedral angle are 2.105 Å and 26.0°, respectively, at the B3LYP/6-311+G(3df) level.<sup>[29]</sup> The value of the dihedral angle shows the large deviation from ca. 90° for unstrained disulfides.<sup>[30]</sup> In this paper we report the reaction of this strained disulfide **16** with Pt<sup>0</sup> complex **2**, where we observed a unique rearrangement caused by the characteristic bicyclic ring system, and we discuss the oxidation of the resulting (dithiolato)Pt<sup>II</sup> complex.



## Results and Discussion

The reaction of disulfide **16** with Pt<sup>0</sup> complex **2** was carried out in CHCl<sub>3</sub> at 0 °C. The <sup>31</sup>P NMR spectrum of the reaction mixture exhibited a singlet at δ 22.0 with satellite signals due to the isotope <sup>195</sup>Pt [<sup>1</sup>J(<sup>195</sup>Pt-<sup>31</sup>P) = 2936 Hz], indicating the formation of a compound having a mirror plane. We assigned the structure of the compound to be the expected (dithiolato)Pt<sup>II</sup> complex **17**. However, the complex **17** was thermally unstable and isomerized gradually at room temperature to another (dithiolato)Pt<sup>II</sup> complex **18**. In the <sup>31</sup>P NMR, compound **18** showed two doublets [<sup>2</sup>J(<sup>31</sup>P-<sup>31</sup>P) = 24 Hz] at δ 20.6 and 21.7 accompanying satellite signals due to the <sup>195</sup>Pt isotope [<sup>1</sup>J(<sup>195</sup>Pt-<sup>31</sup>P) = 2863 and 2929 Hz, respectively]. The <sup>1</sup>H NMR spectrum comprises signals due to four nonequivalent olefinic protons together with four nonequivalent aliphatic protons in the seven-membered ring. The multiplet (δ 2.97-3.10) accompanying satellite signals due to the <sup>195</sup>Pt isotope [<sup>3</sup>J(<sup>195</sup>Pt-<sup>1</sup>H) = 36 Hz] was assigned as those due to the H<sup>6</sup> (see Experimental Section).



The structure of **18** was unambiguously determined by X-ray crystallography (Fig. 1, see also Fig. 4) to be a (cyclohepta-1,3-diene-*cis*-5,6-dithiolato)Pt<sup>II</sup> complex. In the crystal, the cycloheptadiene ring was disordered, and refinement was performed with occupancies of 0.54 and 0.46 for the C(1A)-C(2A)-C(3)-C(4A)-C(5A)-C(6)-C(7A) ring and the C(1B)-C(2B)-C(3)-C(4B)-C(5B)-C(6)-C(7B) ring, respectively, where C(3) and C(6) were common.

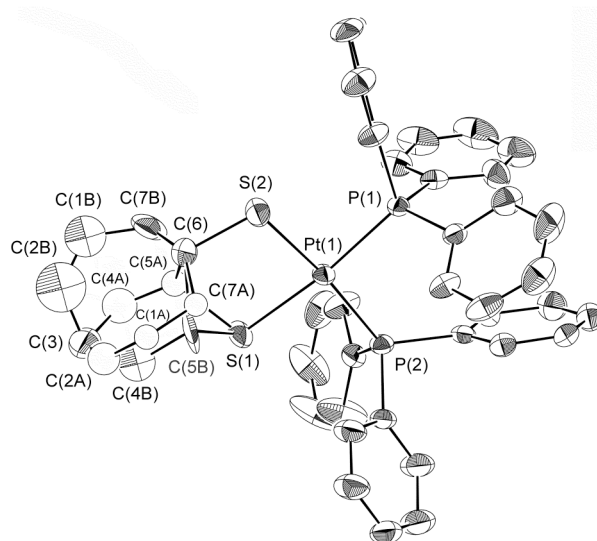
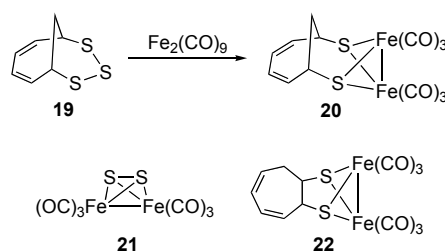


Figure 1. ORTEP drawing of (cyclohepta-1,3-diene-*cis*-5,6-dithiolato)Pt<sup>II</sup> complex **18** (20% ellipsoidal probability). The cycloheptadiene ring is disordered (see also Fig. 4). C(1A), C(1B), C(2A), C(2B), C(4A), C(4B), C(5A), and C(7A) were refined isotropically. Hydrogen atoms and a solvate molecule (CH<sub>2</sub>Cl<sub>2</sub>) are omitted for clarity.

The complex **18** is formed by a [1,5]-sulfur shift of **17**, unprecedented as far as we know, and the *cis* stereochemistry of the two sulfur atoms in **17** is retained. Shaver reported the reaction of trisulfide **19** with Fe<sub>2</sub>(CO)<sub>9</sub> to give the corresponding diiron complex **20**, which decomposed in DMSO at ca. 120 °C.<sup>[31]</sup> On the other hand, Lorenz and coworkers reported the synthesis of **22** by photoreaction of **21** with cycloheptatriene.<sup>[32]</sup> These diiron complexes **20** and **22** correspond to the present Pt<sup>II</sup> complexes **17** and **18**, respectively, but mutual isomerization between **20** and **22** was not reported.



**Oxidation of (dithiolato)Pt<sup>II</sup> complex **18**:** Oxidation of **18** was investigated from the viewpoints of the regio- and stereoselectivities of the oxidation. The oxidation was expected to yield from a maximum number of 4 isomers of monoxides up to the tetraoxide of **18**. Table 1 summarizes results of the oxidation employing from one to four equivalents of dimethyldioxirane (DMD) as the oxidation reagent. The products obtained were (sulfenato-thiolato)Pt<sup>II</sup> complex **23**, (sulfinato-thiolato)Pt<sup>II</sup> complex **24**, (sulfenato-sulfinato)Pt<sup>II</sup> complex **25**, and (disulfinato)Pt<sup>II</sup> complex **26**.

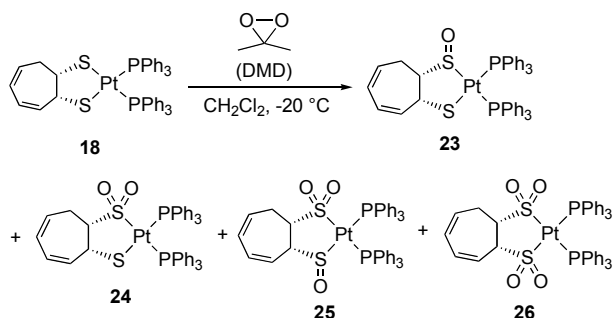


Table 1. Ratios of oxidation products **23-26** and **18** based on <sup>31</sup>P NMR integral ratio. Isolated yields are shown in parentheses.

Run	DMD/equiv	<b>23</b> /%	<b>24</b> /%	<b>25</b> /%	<b>26</b> /%	<b>18</b> /%
1	1.0	10	11	8	4	67
2	2.0	16	28 (22)	17	16 (10)	23 (23)
3	3.0	-	30 (22)	43	21 (21)	6
4	3.5	-	-	47	53	-
5	4.0	-	-	-	100 (87)	-

Among the four products, *S,S*-dioxide **24** and tetraoxide **26** were isolated in pure form, and their structures were determined by X-ray crystallography (Figs. 2 and 3).

The other two, monoxide **23** and trioxide **25**, were not obtained in the pure form by recrystallization of the reaction mixture or by column chromatography because they were unstable on silica gel. Their structures were elucidated on the basis of the <sup>31</sup>P NMR data and the relevant reactions described later. Table 2 summarizes the <sup>31</sup>P NMR data of **18** and **23-26**. One of the two <sup>1</sup>*J*<sub>Pt-P</sub> coupling constants of **23** (2398 Hz) was much smaller than the other (3057 Hz), the latter of which is comparable to those of (dithiolato)Pt<sup>II</sup> complex **18** (2863 and 2929 Hz). The sets of <sup>1</sup>*J*<sub>Pt-P</sub> coupling constants of representative (sulfenato-thiolato)Pt<sup>II</sup> complexes **3**, **9b**, and **11** are reported to be (2281 and 3201 Hz),<sup>[2]</sup> (2451 and 3587 Hz),<sup>[11]</sup> and (2295 and 3542 Hz),<sup>[12]</sup> respectively. Thus, the set (2398 and 3057 Hz) of **23** is consistent with the presence of a sulfenato substituent that has stronger trans influence than that of thiolato substituents.<sup>[2-12]</sup> The regiochemistry of the oxygen atom in **23** is assigned as shown because *S,S*-dioxide **24** must be formed by successive oxidation of **23**. The stereochemistry of the S=O group in **23** is not clear at present.

In the case of trioxide **25**, the signals centered at δ 11.3 with 2881 Hz of the <sup>1</sup>*J*<sub>Pt-P</sub> coupling constant is assignable to those due to the <sup>31</sup>P atom being *trans* to the -SO<sub>2</sub>- group, though the value is larger by 117-327 Hz than those of **24** (2554 Hz) and **26** (2662 and 2764 Hz). The other <sup>31</sup>P atom *trans* to the sulfenato substituent has 2404 Hz of the <sup>1</sup>*J*<sub>Pt-P</sub> coupling constant, which is comparable to that

in **23** (2398 Hz). That **25** is a trioxide of **18** is verified by the following experiment: oxidation of dioxide **24** with DMD at -20 °C produced **25** in 13% yield together with tetraoxide **26** (44%) and **24** (43%).

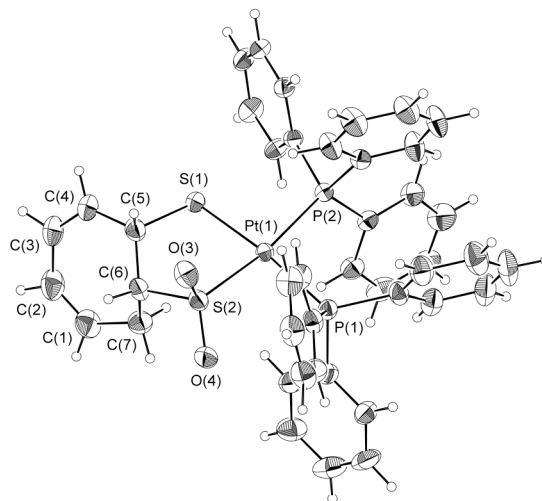


Figure 2. ORTEP drawing of (sulfinato-thiolato)Pt<sup>II</sup> complex **24** (30% ellipsoidal probability).

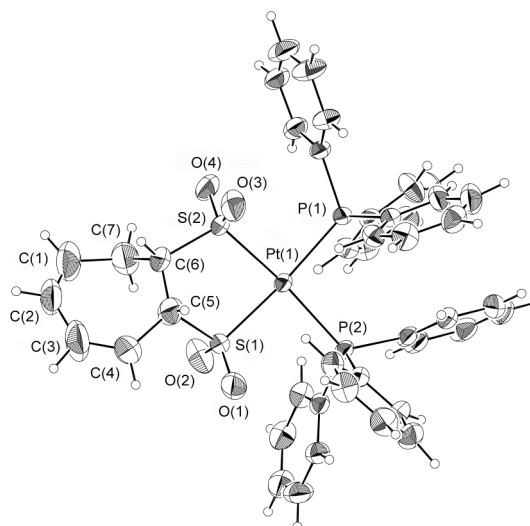
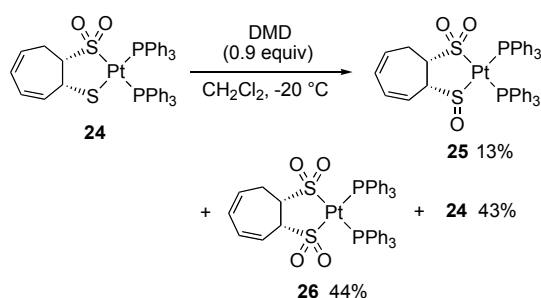


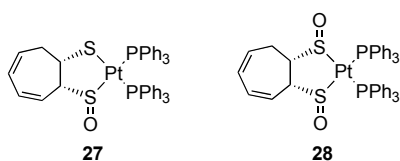
Figure 3. ORTEP drawing of (disulfinato)Pt<sup>II</sup> complex **26** (30% ellipsoidal probability).

Table 2. <sup>31</sup>P NMR data of **18** and oxidation products **23-26**.

	(X,Y)	δ ( <sup>1</sup> <i>J</i> <sub>Pt-P</sub> /Hz)	<sup>2</sup> <i>J</i> <sub>P-P</sub> /Hz
<b>18</b>	(S,S)	20.6 (2863), 21.7 (2929)	24
<b>23</b>	(SO,S)	16.9 (2398), 17.8 (3057)	29
<b>24</b>	(SO <sub>2</sub> ,S)	13.8 (2554), 18.9 (3045)	25
<b>25</b>	(SO <sub>2</sub> ,SO)	11.3 (2881), 14.9 (2404)	27
<b>26</b>	(SO <sub>2</sub> ,SO <sub>2</sub> )	12.5 (2662), 13.8 (2764)	22



In the oxidation of (dithiolato)Pt<sup>II</sup> complex **18** with DMD, the formation of either another monoxide **27** or S,S'-dioxide **28** was not observed, indicating that the first oxidation took place regioselectively and the second oxidation occurred exclusively at the sulfenato sulfur atom of **23**. This regioselectivity in the first step is discussed later in this paper. A reactivity similar to that of **23** has been reported for a kind of thiolato complexes by Schenk et al.<sup>[33]</sup> In the oxidation of CpRuL<sub>2</sub>(SR) (Cp = cyclopentadienyl; L<sub>2</sub> = 2PPh<sub>3</sub>, dppe, or CO/PPh<sub>3</sub>, R = Me, Ph, or PhCH<sub>2</sub>) with DMD, the initial oxidation product CpRuL<sub>2</sub>[S(O)R] underwent the second oxidation much faster than the starting complex, and the only detectable product was CpRuL<sub>2</sub>(SO<sub>2</sub>R) even when 1 molar equivalent of DMD was employed. Schenk proposed that transition metal sulfenates might be expected to be very good nucleophiles if the excellent  $\pi$ -donor ability of low-valent transition metal fragments was taken into account,<sup>[33]</sup> which is true for the present case.



**Crystal structures of 18, 24, and 26:** Table 3 summarizes the relevant bond lengths, bond angles, and dihedral angles of **18**, **24**, and **26**. Pt(1)-S(1) and Pt(1)-S(2) bond lengths are not influenced largely by the oxidation state of the sulfur atoms, and are in the narrow range of 2.2990(15) (**26**) - 2.339(4) (**18**) Å. The Pt-P bond lengths *trans* to the sulfinato ligand [Pt(1)-P(2) 2.3249(12) Å in **24** and Pt(1)-P(1) 2.3520(15) and Pt(1)-Pt(2) 2.3660(15) Å in **26**] are longer than those *trans* to the thiolato ligand [2.275(3)-2.3055(12) Å for those in **18** and Pt(1)-P(1) in **24**] owing to the stronger trans influence of the sulfinato ligand.<sup>[1-7,11,12]</sup> The S-O bond lengths are almost similar to each other.

Table 3. Relevant bond lengths (Å), bond angles (deg), and dihedral angles (deg) data of **18**, **24**, and **26**.

	<b>18</b> <sup>[a]</sup>	<b>24</b>	<b>26</b>
Pt(1)-S(1)	2.339(4)	2.3130(12)	2.2990(15)
Pt(1)-S(2)	2.308(4)	2.3283(12)	2.3017(17)
Pt(1)-P(1)	2.275(3)	2.3055(12)	2.3520(15)
Pt(1)-P(2)	2.296(3)	2.3249(12)	2.3660(15)
S(1)-O(1)	-	-	1.424(6)
S(1)-O(2)	-	-	1.402(8)
S(2)-O(3)	-	1.470(4)	1.452(7)
S(2)-O(4)	-	1.444(4)	1.438(7)
C(5)-C(6)	[b]	1.506(7)	1.451(12)
S(1)-C(5)	[b]	1.858(5)	1.849(10)
S(2)-C(6)	[b]	1.801(5)	1.808(8)

S(1)-Pt(1)-S(2)	88.96(13)	85.70(4)	85.25(6)
S(2)-Pt(1)-P(1)	87.25(12)	89.08(4)	90.71(6)
P(1)-Pt(1)-P(2)	98.50(11)	97.17(4)	96.11(6)
P(2)-Pt(1)-S(1)	85.50(12)	88.37(4)	88.48(6)
sum of the above four bond angles	360.21	360.32	360.01
P(1)-Pt(1)-S(1)	172.50(15)	173.91(4)	174.57(6)
P(2)-Pt(1)-S(2)	174.01(12)	171.01(4)	168.31(6)

S(1)-C(5)-C(6)-S(2)	[b]	-59.4(3)	-47.7(5)
C(4)-C(5)-C(6)-C(7)	[b]	-60.2(6)	48.1(10)

[a] The values on **18** are mean values of two disordered structures. [b] Because of the disorder of the cycloheptadiene ring in **18**, the values are excluded for discussion.

**Regioselectivity on oxidation of 18:** The oxidation of **18** with DMD took place at the sulfur atom assigned as S(2) in Fig.1. This regioselectivity would be explained not by an electronic reason but a steric reason around the sulfur atoms S(1) and S(2): The electronic nature of two sulfur atoms in **18** is considered to be almost similar, because *trans* substituents of the two sulfur atoms to the Pt atom are the same phosphine ligand that provides the same trans influence. In addition, it is hard to emphasize the difference of inductive effects brought about by the allylic substituent for the S(1) and the homo-allylic one for the S(2).

Although the platinadithiabicyclo[5.3.0]decadiene ring moiety of **18** was disordered in the crystalline state as depicted in Fig.1, we can divide the moiety into two components (Fig.4). Both the C<sub>2</sub>S<sub>2</sub>Pt five-membered rings, C(5A)-S(1)-Pt(1)-S(2)-C(6) [Fig.4(a)] and C(5B)-S(1)-Pt(1)-S(2)-C(6) [Fig.4(b)], take a distorted envelope conformation with the C(5A) and the C(5B) at the flap position, respectively. The common dihedral angle S(1)-Pt(1)-S(2)-C(6) is 11.8(6)°. For reference, the C<sub>2</sub>S<sub>2</sub>Pt ring in tetraoxide **26** takes an envelope conformation where the C(5) possesses the flap position and the S(1)-Pt(1)-S(2)-C(6) dihedral angle is 0.2(3)°, and the ring in **24** takes a slightly distorted envelope conformation with the C(6) at the flap position and 4.2(2)° of the S(2)-Pt(1)-S(1)-C(5) dihedral angle. An important difference between the two envelope structures of **24** and **26** is the position of the S(2) atom which is oxidized by DMD in the first step in the case of **18**; in **26**, the S(2) atom resides on the base line of the envelope, and in **24** the S(2) atom rides on the folding line of the envelope. In this respect, the five-membered ring in **18** takes a conformation similar to that of **26**. DFT calculations<sup>[29]</sup> were carried out on a model compound **29**, employing the two types of envelope conformations of **24** and **26** as the initial structures.<sup>[34]</sup> As the results, the two calculations gave the same optimized structure, which is very similar to that of **18** (Fig. 5).

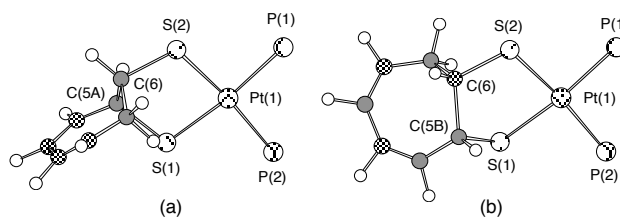


Figure 4. Two components of **18** in the crystalline state (PPh<sub>3</sub> ligands are omitted for clarity) [S(1)-Pt(1)-S(2)-C(6) 11.8(6)°].

## Experimental Section

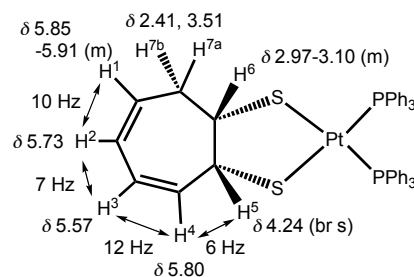
**General:** The melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected.  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra were determined on Bruker AM400 or DRX400 (400 and 162 MHz, respectively) spectrometers using  $\text{CDCl}_3$  as the solvent at  $25^\circ\text{C}$ , unless otherwise noted. IR spectra were taken on a Perkin Elmer System 2000 FT-IR spectrometer. Elemental analysis was performed by the Molecular Analysis and Life Science Center of Saitama University. Column chromatography was performed with silica gel (70–230 mesh); the eluent is shown in parentheses. An acetone solution of dimethyldioxirane (DMD) was prepared by oxidation of acetone with Oxone<sup>®</sup> (Sigma-Aldrich).<sup>[35]</sup>

**Reaction of Disulfide 16 with  $(\text{Ph}_3\text{P})_2\text{Pt}(\eta^2\text{-C}_2\text{H}_4)$  (2):** A solution of disulfide **16** (11.0 mg, 0.0704 mmol) in chloroform (2 mL) was added to a solution of  $(\text{Ph}_3\text{P})_2\text{Pt}(\eta^2\text{-C}_2\text{H}_4)$  (**2**) (51.8 mg, 0.0693 mmol) in chloroform (3 mL) under argon at  $0^\circ\text{C}$  over 5 min. The mixture was stirred for 15 min at  $0^\circ\text{C}$ , and the solvent was removed under reduced pressure. The  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra of the residue showed the formation of (dithiolato) $\text{Pt}^{\text{II}}$  complex **17**. The complex **17** was not obtained as a pure form by column chromatography ( $R_f = 0.25$ ,  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{OH}$  5/1).

**(Cyclohepta-1,3-diene-*cis*-5,7-dithiolato)bis(triphenylphosphane)platinum (17):**  $^1\text{H}$  NMR  $\delta$  1.80 (br s, 2H), 3.25 (br s, 2H), 5.77–5.81 (m, 2H), 6.19 (ddd,  $J = 9.1, 6.4, 3.2$  Hz, 2H), 7.11–7.47 (m, 30H);  $^{31}\text{P}$  NMR  $\delta$  22.0 [s,  $^1J(^{195}\text{Pt}-^{31}\text{P}) = 2936$  Hz].

**Isomerization of 17 to (Dithiolato) $\text{Pt}^{\text{II}}$  Complex 18:** A solution of the above mixture in chloroform was stirred for 24 h at room temperature. The mixture was evaporated to dryness, and the residue was subjected to column chromatography (dichloromethane/ether 5/1) to give **18** ( $R_f = 0.4$ ; 47.8 mg, 79%).

**(Cyclohepta-1,3-diene-*cis*-5,6-dithiolato)bis(triphenylphosphane)platinum (18):** pale yellow crystals, m.p.  $224\text{--}226^\circ\text{C}$  decomp (hexane/ $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR  $\delta$  2.41 (pseudo dd,  $J = 16.2, 8.5$  Hz, 1H,  $\text{H}^{\text{a}}$  or  $\text{H}^{\text{b}}$ ), 2.97–3.10 [m,  $^3J(^{195}\text{Pt}-^1\text{H}) = 36$  Hz, 1H,  $\text{H}^{\text{c}}$ ], 3.51 (pseudo dd,  $J = 14.6, 12.4$  Hz, 1H,  $\text{H}^{\text{a}}$  or  $\text{H}^{\text{b}}$ ), 4.24 (br s, 1H,  $\text{H}^{\text{d}}$ ), 5.57 (dd,  $J = 11.8, 6.9$  Hz, 1H,  $\text{H}^{\text{e}}$ ), 5.73 (ddd,  $J = 10.4, 7.3, 2.8$  Hz, 1H,  $\text{H}^{\text{e}}$ ), 5.80 (dd,  $J = 11.7, 5.7$  Hz, 1H,  $\text{H}^{\text{d}}$ ), 5.85–5.91 (m, 1H,  $\text{H}^{\text{f}}$ ), 7.12–7.16 (m, 12H), 7.24–7.29 (m, 6H), 7.40–7.52 (m, 12H);  $^{31}\text{P}$  NMR  $\delta$  20.6 [d,  $^2J(^{31}\text{P}-^{31}\text{P}) = 24$  Hz,  $^1J(^{195}\text{Pt}-^{31}\text{P}) = 2863$  Hz], 21.7 [d,  $^2J(^{31}\text{P}-^{31}\text{P}) = 24$  Hz,  $^1J(^{195}\text{Pt}-^{31}\text{P}) = 2929$  Hz]. Anal. Calcd for  $\text{C}_{43}\text{H}_{38}\text{P}_2\text{PtS}_2$ : C 58.96, H 4.37. Found: C 58.66, H 4.35. The assignment of the  $^1\text{H}$  NMR data is based on the H-H COSY NMR experiment. Data for the seven-membered ring in **18** are summarized as below.



### Oxidation of (Dithiolato) $\text{Pt}^{\text{II}}$ Complex 18 with DMD

**(1) With 1 equiv of DMD:** An acetone solution of DMD (0.13 M, 0.14 mL, 0.018 mmol) was added to a solution of **18** (15.4 mg, 0.0176 mmol) in dichloromethane (2 mL) at  $-20^\circ\text{C}$  under argon. After stirring for 2 h at this temperature, the solvent was removed under reduced pressure at  $-20^\circ\text{C}$ . The  $^{31}\text{P}$  NMR of the residue showed the formation of (sulfenato-thiolato) $\text{Pt}^{\text{II}}$  complex **23** (10%), (sulfinato-thiolato) $\text{Pt}^{\text{II}}$  complex **24** (11%), (sulfenato-sulfinato) $\text{Pt}^{\text{II}}$  complex **25** (8%), (disulfinato) $\text{Pt}^{\text{II}}$  complex **26** (4%), and **18** (67%).

**(2) With 2 equiv of DMD:** In a similar manner, a solution of **18** (21.5 mg, 0.0245 mmol) in dichloromethane (3 mL) was treated with DMD (0.079 M, 0.62 mL, 0.049 mmol) at  $-20^\circ\text{C}$ . The  $^{31}\text{P}$  NMR of the reaction mixture showed the formation of (sulfenato-thiolato) $\text{Pt}^{\text{II}}$  complex **23** (16%), (sulfinato-thiolato) $\text{Pt}^{\text{II}}$  complex **24** (28%), (sulfenato-sulfinato) $\text{Pt}^{\text{II}}$  complex **25** (17%), (disulfinato) $\text{Pt}^{\text{II}}$  complex **26** (17%), and **18** (23%). The mixture was subjected to column chromatography (dichloromethane/ether 4/1) to give **24** ( $R_f = 0.5$ ; 4.8 mg, 22%), **26** ( $R_f = 0.3$ ; 2.3 mg, 10%) and **18** (4.8 mg, 23%). Complexes **23** and **25** decomposed in the column.

**(3) With 3 equiv of DMD:** In a similar manner, a solution of **18** (21.8 mg, 0.0249 mmol) in dichloromethane (3 mL) was treated with DMD (0.079 M, 0.92 mL, 0.073 mmol) at  $-20^\circ\text{C}$ . The  $^{31}\text{P}$  NMR of the reaction mixture showed the formation of (sulfinato-thiolato) $\text{Pt}^{\text{II}}$  complex **24** (30%), (sulfenato-sulfinato) $\text{Pt}^{\text{II}}$  complex **25** (43%), (disulfinato) $\text{Pt}^{\text{II}}$  complex **26** (21%), and **18** (6%). The mixture was subjected to column chromatography (dichloromethane/ether 4/1) to give **24** (5 mg, 22%) and **26** (4.8 mg, 21%). Complex **25** decomposed in the column.

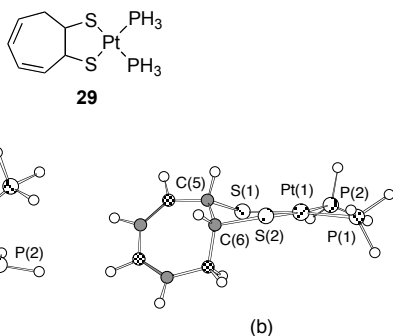


Figure 5. The optimized structure of **29** by DFT calculations: (a) top view; (b) side view;  $\text{S}(1)\text{--Pt}(1)\text{--S}(2)\text{--C}(6)$   $9.5^\circ$ . Other relevant bond lengths (Å) and angles (deg):  $\text{Pt}(1)\text{--S}(1)$  2.400,  $\text{Pt}(1)\text{--S}(2)$  2.405,  $\text{Pt}(1)\text{--P}(1)$  2.402,  $\text{Pt}(1)\text{--P}(2)$  2.396,  $\text{S}(1)\text{--C}(5)$  1.951,  $\text{S}(2)\text{--C}(6)$  1.929,  $\text{C}(1)\text{--C}(2)$  1.351,  $\text{C}(2)\text{--C}(3)$  1.461,  $\text{C}(3)\text{--C}(4)$  1.353,  $\text{C}(4)\text{--C}(5)$  1.496,  $\text{C}(5)\text{--C}(6)$  1.524,  $\text{C}(6)\text{--C}(7)$  1.538,  $\text{S}(1)\text{--Pt}(1)\text{--S}(2)$  88.6,  $\text{S}(2)\text{--Pt}(1)\text{--P}(1)$  86.4,  $\text{P}(1)\text{--Pt}(1)\text{--P}(2)$  98.7,  $\text{P}(2)\text{--Pt}(1)\text{--S}(1)$  174.0,  $\text{P}(1)\text{--Pt}(1)\text{--S}(2)$  174.0,  $\text{C}(4)\text{--C}(5)\text{--C}(6)\text{--C}(7)$  58.3.

As shown in Fig.6, DMD approaches the sulfur atoms from axial directions of the five-membered ring. The approach of DMD from the endo side of the seven-membered ring to S(1) and S(2) atoms is substantially hindered by the axial  $\text{CH}_2$  group bound to C(6). The axial hydrogen at C(5) disturbs the attack of DMD at the neighboring S(1) from the exo side of the seven-membered ring. Thus, the feasible, least hindered attack of DMD is that at S(2) from the exo side of the seven-membered ring to give **23**. On this consideration, the stereochemistry of the  $\text{S}=\text{O}$  group in **23** is exo to the cycloheptadiene ring. In the second oxidation, monoxide **23** may change the conformation and, more importantly, the electronic effect mentioned above allows DMD to attack at S(2) again to give **24**. In **24**, the sulfur atom to undergo oxidation [S(1)] is located at the baseline of the envelope conformation, and the position is favorable for the approach of DMD as discussed above.

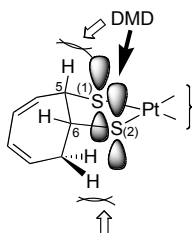


Figure 6. Attack of DMD to sulfur atoms of **18** (**29**) from axial directions.

## Conclusion

We found that the reaction of bicyclic disulfide **16** with  $(\text{Ph}_3\text{P})_2\text{Pt}(\eta^2\text{-C}_2\text{H}_4)$  (**2**) yielded the corresponding (dithiolato) $\text{Pt}^{\text{II}}$  complex **17** by oxidative addition and that **17** isomerized to another (dithiolato) $\text{Pt}^{\text{II}}$  complex **18** at room temperature by a [1,5]-sulfur rearrangement in the cycloheptadiene ring. Oxidation of **18** with DMD was investigated in detail. The reaction furnished (sulfenato-thiolato)- (**23**), (sulfinato-thiolato)- (**24**), (sulfenato-sulfinato)- (**25**), and (disulfinato) $\text{Pt}^{\text{II}}$  (**26**) complexes. The structures of **24** and **26** were determined unambiguously by X-ray crystallography, where we observed a difference in two envelope forms of their  $\text{C}_2\text{S}_2\text{Pt}$  five-membered rings. The oxidation of **18** to monoxide **23** took place regioselectively, which is explained in terms of a steric reason on the basis of the structure obtained by X-ray crystallography and DFT calculations. The oxidation of **23** occurred at not the thiolato sulfur atom but the sulfenato sulfur atom to give  $S,S$ -dioxide **24**.

**(4) With 3.5 equiv of DMD:** In a similar manner, a solution of **18** (25.3 mg, 0.0289 mmol) in dichloromethane (3 mL) was treated with DMD (0.077 M, 1.3 mL, 0.10 mmol) at -20 °C. The  $^{31}\text{P}$  NMR of the reaction mixture showed the formation of (sulfenato-sulfinato) $\text{Pt}^{\text{II}}$  complex **25** (47%) and (disulfinato) $\text{Pt}^{\text{II}}$  complex **26** (53%).

**(5) With 4 equiv of DMD:** In a similar manner, a solution of **18** (22.7 mg, 0.0259 mmol) in dichloromethane (3 mL) was treated with DMD (0.0791 M, 1.35 mL, 0.107 mmol) at -20 °C. The  $^{31}\text{P}$  NMR of the reaction mixture showed the formation of (disulfinato) $\text{Pt}^{\text{II}}$  complex **26** only as the complex. The mixture was subjected to column chromatography (dichloromethane/ether 4/1) to give **26** (21.2 mg, 87%).

**(Cyclohepta-1,3-diene-*cis*-6-sulfenato-5-thiolato)bis(triphenylphosphane)platinum (23):**  $^{31}\text{P}$  NMR  $\delta$  16.9 [d,  $^2J(^{31}\text{P}-^{31}\text{P}) = 29$  Hz,  $^1J(^{195}\text{Pt}-^{31}\text{P}) = 2398$  Hz], 17.8 [d,  $^2J(^{31}\text{P}-^{31}\text{P}) = 29$  Hz,  $^1J(^{195}\text{Pt}-^{31}\text{P}) = 3057$  Hz].

**(Cyclohepta-1,3-diene-*cis*-6-sulfinato-5-thiolato)bis(triphenylphosphane)platinum (24):** orange crystals, m.p. 225–227 °C decomp (EtOH/ $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR  $\delta$  2.65–2.80 [m,  $^3J(^{195}\text{Pt}-^1\text{H}) = 24$  Hz, 1H], 2.85–2.92 (m, 1H), 2.98–3.05 (m, 1H), 4.19 (br s, 1H), 5.67 (dd,  $J = 11.7, 6.9$  Hz, 1H), 5.84 (ddd,  $J = 10.2, 7.2, 2.7$  Hz, 1H), 5.91 (dd,  $J = 11.8, 5.6$  Hz, 1H), 6.04–6.10 (m, 1H), 7.14–7.19 (m, 12H), 7.29–7.34 (m, 6H), 7.37–7.52 (m, 12H);  $^{31}\text{P}$  NMR  $\delta$  13.8 [d,  $^2J(^{31}\text{P}-^{31}\text{P}) = 25$  Hz,  $^1J(^{195}\text{Pt}-^{31}\text{P}) = 2554$  Hz], 18.9 [d,  $^2J(^{31}\text{P}-^{31}\text{P}) = 25$  Hz,  $^1J(^{195}\text{Pt}-^{31}\text{P}) = 3045$  Hz]; IR (KBr) 1206, 1052  $\text{cm}^{-1}$  ( $\text{SO}_2$ ). Anal. Calcd for  $\text{C}_{43}\text{H}_{38}\text{O}_2\text{P}_2\text{PtS}_2$ : C 56.88, H 4.22. Found: C 56.62, H 4.15.

**(Cyclohepta-1,3-diene-*cis*-5-sulfenato-6-sulfinato)bis(triphenylphosphane)platinum (25):**  $^1\text{H}$  NMR  $\delta$  2.75–2.84 (m, 1H), 3.11–3.28 [m,  $^3J(^{195}\text{Pt}-^1\text{H}) = 25$  Hz, 1H], 3.75–3.85 (m, 1H), 3.87 (br s, 1H), 5.85 (dd,  $J = 11.7, 6.4$  Hz, 1H), 5.90–5.98 (m, 1H), 5.99–6.06 (m, 1H), 6.16 (dd,  $J = 11.5, 7.0$  Hz, 1H), 7.15–7.26 (m, 12H), 7.32–7.39 (m, 12H), 7.53–7.58;  $^{31}\text{P}$  NMR  $\delta$  11.3 [d,  $^2J(^{31}\text{P}-^{31}\text{P}) = 27$  Hz,  $^1J(^{195}\text{Pt}-^{31}\text{P}) = 2881$  Hz], 14.9 [d,  $^2J(^{31}\text{P}-^{31}\text{P}) = 27$  Hz,  $^1J(^{195}\text{Pt}-^{31}\text{P}) = 2404$  Hz].

**(Cyclohepta-1,3-diene-*cis*-5,6-disulfinato)bis(triphenylphosphane)platinum (26):** pale yellow crystals, m.p. 176–179 °C decomp (EtOH/ $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR  $\delta$  2.08–2.12 (m, 1H), 2.80–2.86 (m, 1H), 3.06–3.14 (m, 1H), 4.34 (br s, 1H), 5.93 (ddd,  $J = 10.4, 7.3, 2.8$  Hz, 1H), 5.99–6.05 (m, 2H), 6.23 (dd,  $J = 11.9, 7.0$  Hz, 1H), 7.16–7.25 (m, 12H), 7.28–7.33 (m, 6H), 7.35–7.41 (m, 6H), 7.47–7.53 (m, 6H);  $^{31}\text{P}$  NMR  $\delta$  12.5 [d,  $^2J(^{31}\text{P}-^{31}\text{P}) = 22$  Hz,  $^1J(^{195}\text{Pt}-^{31}\text{P}) = 2662$  Hz], 13.8 [d,  $^2J(^{31}\text{P}-^{31}\text{P}) = 22$  Hz,  $^1J(^{195}\text{Pt}-^{31}\text{P}) = 2764$  Hz]; IR (KBr) 1225, 1052  $\text{cm}^{-1}$  ( $\text{SO}_2$ ). Anal. Calcd for  $\text{C}_{44}\text{H}_{40}\text{Cl}_2\text{O}_4\text{P}_2\text{PtS}_2$  ( $\text{C}_{43}\text{H}_{38}\text{O}_4\text{P}_2\text{PtS}_2 \cdot \text{CH}_2\text{Cl}_2$ ): C 51.57, H 3.93. Found: C 51.84, H 3.89.

**X-ray crystallography:** Mac Science DIP3000 diffractometer with a graphite-monochromated Mo- $\text{K}\alpha$  radiation ( $\lambda = 0.71073$  Å). The data reduction was made by the Maxus program system. Absorption corrections were done by a multi-scan method (SORTAV<sup>[36]</sup>). The structure was solved with a direct method (SIR97<sup>[37]</sup> or DIRDIF<sup>[38]</sup>) and refined with full-matrix least-squares (SHELXL-97<sup>[39]</sup>) using all independent reflections. Non-hydrogen atoms were analyzed anisotropically and hydrogen atoms were placed at calculated positions, unless otherwise noted.

**Crystal Data for 18:**  $\text{C}_{43}\text{H}_{38}\text{O}_2\text{P}_2\text{PtS}_2 \cdot \text{CH}_2\text{Cl}_2$ ,  $M_s = 960.87$ , yellow plate,  $0.26 \times 0.14 \times 0.10$  mm<sup>3</sup>, monoclinic,  $P2_1/c$ ,  $a = 13.4020(10)$  Å,  $b = 9.8730(7)$  Å,  $c = 32.167(3)$  Å,  $\beta = 109.249(18)^\circ$ ,  $V = 4018.3(6)$  Å<sup>3</sup>,  $\rho_{\text{calcd}} = 1.448$  g cm<sup>-3</sup>,  $Z = 4$ ,  $\mu(\text{Mo}-\text{K}\alpha) = 3.840$  cm<sup>-1</sup>. Intensity data of 7875 unique reflections were collected in the range of  $-16 \leq h \leq 14$ ,  $-11 \leq k \leq 11$ ,  $-40 \leq l \leq 41$ .  $R1 = 0.0752$  ( $I \geq 2\sigma I$ , 4285 reflections),  $wR2 = 0.1879$  (for all), and  $\text{GOF} = 1.044$ , 461 parameters; max/min residual electron density =  $1.142/-0.970$  e Å<sup>-3</sup>. Carbon atoms C(1A), C(1B), C(2A), C(2B), C(4A), C(4B), C(5A), and C(7A) were refined isotropically.

**Crystal Data for 24:**  $\text{C}_{43}\text{H}_{38}\text{O}_2\text{P}_2\text{PtS}_2$ ,  $M_s = 907.941$ , orange plate,  $0.36 \times 0.36 \times 0.26$  mm<sup>3</sup>, monoclinic,  $P2_1/c$ ,  $a = 15.3910(4)$  Å,  $b = 13.1450(4)$  Å,  $c = 20.2431(9)$  Å,  $\beta = 112.995(18)^\circ$ ,  $V = 3770.1(2)$  Å<sup>3</sup>,  $\rho_{\text{calcd}} = 1.600$  g cm<sup>-3</sup>,  $Z = 4$ ,  $\mu(\text{Mo}-\text{K}\alpha) = 3.954$  cm<sup>-1</sup>. Intensity data of 7926 unique reflections were collected in the range of  $-19 \leq h \leq 19$ ,  $-16 \leq k \leq 16$ ,  $-24 \leq l \leq 25$ .  $R1 = 0.0397$  ( $I \geq 2\sigma I$ , 7088 reflections),  $wR2 = 0.1109$  (for all), and  $\text{GOF} = 1.076$ , 452 parameters; max/min residual electron density =  $2.648/-1.002$  e Å<sup>-3</sup>.

**Crystal Data for 26:**  $\text{C}_{43}\text{H}_{38}\text{O}_4\text{P}_2\text{PtS}_2$ ,  $M_s = 939.94$ , pale yellow,  $0.18 \times 0.16 \times 0.12$  mm<sup>3</sup>, monoclinic,  $P2_1/c$ ,  $a = 12.7380(4)$  Å,  $b = 20.9550(7)$  Å,  $c = 16.9978(7)$  Å,  $\beta = 123.561(1)^\circ$ ,  $V = 3780.8(2)$  Å<sup>3</sup>,  $\rho_{\text{calcd}} = 1.651$  g cm<sup>-3</sup>,  $Z = 4$ ,  $\mu(\text{Mo}-\text{K}\alpha) = 3.950$  cm<sup>-1</sup>. Intensity data of 7433 unique reflections were collected in the range of  $-16 \leq h \leq 16$ ,  $-26 \leq k \leq 26$ ,  $-17 \leq l \leq 18$ .  $R1 = 0.0439$  ( $I \geq 2\sigma I$ , 6456 reflections),  $wR2 = 0.1241$  (for all), and  $\text{GOF} = 1.141$ , 470 parameters; max/min residual electron density =  $1.212/-0.985$  e Å<sup>-3</sup>.

CCDC-628607 (**18**), CCDC-628608 (**24**), and CCDC-628609 (**26**) contain the supplementary crystallographic data. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223 336-033; E-mail: deposit@ccdc.cam.ac.uk].

**Oxidation of (Sulfinato-thiolato) $\text{Pt}^{\text{II}}$  Complex 24:** An acetone solution of DMD (0.077 M, 0.18 mL, 0.014 mmol) was added to a solution of **24** (14.5 mg, 0.0160 mmol) in dichloromethane (2 mL) at -20 °C under argon, and the mixture was stirred for 1.5 h at this temperature. The solvent was removed under reduced pressure at -20 °C. The  $^{31}\text{P}$

NMR spectrum of the residue showed the formation of **25**, **26**, and **24** in a ratio of 13:44:43.

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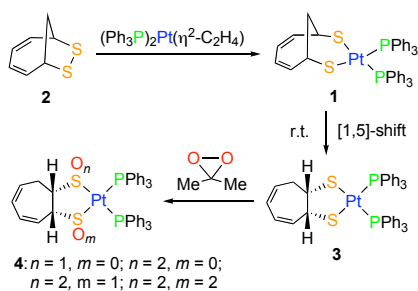
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## Platinum-Sulfur Complexes

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**Rearrangement of a (Dithiolato)Pt<sup>II</sup> Complex Formed by Reaction of a Cyclic Disulfide, 5,6-Dithiabicyclo[4.2.1]nona-1,3-diene, with a Platinum(0) Complex. Oxidation of the Rearranged (Dithiolato)Pt<sup>II</sup> Complex**



### Rearrangement and oxidation:

[1,5]-Sulfur rearrangement took place on a (dithiolato)Pt<sup>II</sup> complex, formed by the reaction of a strained bicyclic disulfide with  $(\text{Ph}_3\text{P})_2\text{Pt}(\eta^2\text{-C}_2\text{H}_4)$ , to give another (dithiolato)Pt<sup>II</sup> complex. The oxidation of the latter with dimethyldioxirane provided the corresponding four oxides, where regioselectivity and chemoselectivity were observed.