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# Rearrangement of a (Dithiolato)platinum(II) Complex Formed by Reaction of Cyclic Disulfide 7,8-Dithiabicyclo[4.2.1]nona-2,4-diene with a Platinum(0) Complex: Oxidation of the Rearranged (Dithiolato)platinum(II) Complex

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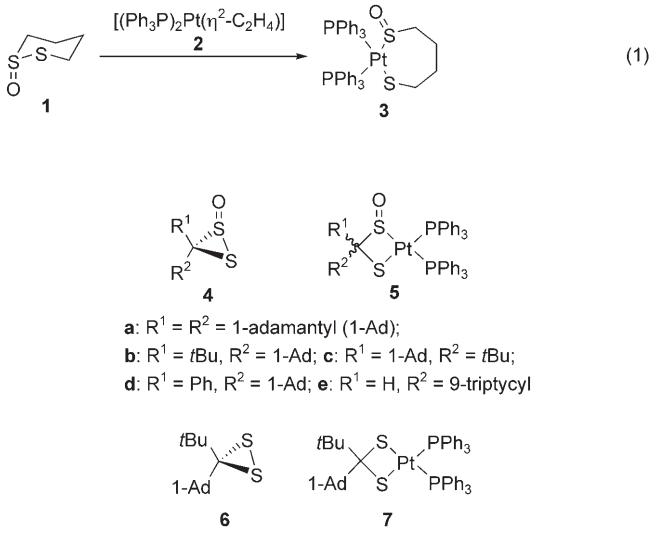
**Abstract:** Reaction of the title bicyclic disulfide **16** with $[(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)]$ (**2**) yielded the corresponding (dithiolato)platinum(II) complex **17** by oxidative addition. The initial product **17** isomerized at room temperature in a [1,5]-sulfur rearrangement to give another (dithiolato)platinum(II) complex **18** in high isolated yield. Oxidation reactions of **18** with dimethyldioxirane (DMD) provided (sulfenato-thiolato)-platinum(II) **23**, (sulfinato-thiolato)platinum(II) **24**, (sulfenato-sulfinato)platinum(II) **25**, and (disulfinato)platinum(II) **26** complexes, the structures of which were elucidated by NMR spectroscopy and X-ray crystallography. The oxidation process took place regioselectively in the first step and chemoselectively in the second. The selectivities are discussed.

**Keywords:** platinum · X-ray diffraction · density functional calculations · disulfides · oxidation · rearrangement

## Introduction

The oxidative addition of a sulfur–sulfur bond within cyclic sulfur compounds to platinum(0) complexes is currently a topic of research interest.[1–11] Weigand and co-workers reported that the reaction of dithiane 1-oxide **1** with $[(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)]$ (**2**) gave (sulfenato-thiolato)platinum(II) complex **3** in high yield [Eq. (1)].[2–7] This reaction has been applied to three-membered cyclic thiosulfinates, dithiirane 1-oxides **4**, and the reaction of **4** with **2** yielded the corresponding four-membered (sulfenato-thiolato)platinum(II) complexes **5** in high yields.[8,9] We have also found that the reaction of dithiirane **6** with **2** provided the (dithiolato)platinum(II) complex **7**.[10]

Woollins and co-workers examined the reactions of **8a** and its oxides **8b–e** with $[Pt(PPh_3)_4]$, which led to the corresponding $Pt^{II}$ complex **9a** and its monoxide to tetraoxide derivatives **9b–e**, respectively. These complexes were characterized by X-ray crystallography and NMR spectroscopy, in particular $^{31}P$ NMR spectroscopy.[11] They also reported the reaction of **10a–d** with $[Pt(PPh_3)_4]$ which gives rise to the corresponding platinum complex **11**.[12]




(1)

*S*-Oxides of (dithiolato)platinum(II) complexes can also be prepared by their oxidation.[13–15] Photo-oxidation of (diimino-dithiolato)platinum(II) complex **12** with molecular oxygen yielded (sulfinato-thiolato)platinum(II) **13** and (disulfinato)$Pt^{II}$ complexes **14** [Eq. (2)].[14] The oxidation of **13** with excess $H_2O_2$ also gave **14**.[15] However, the oxidation re-

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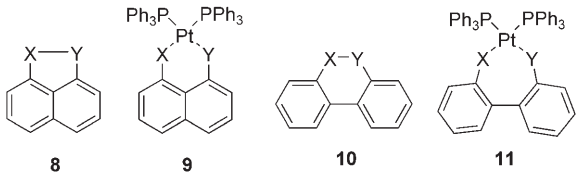
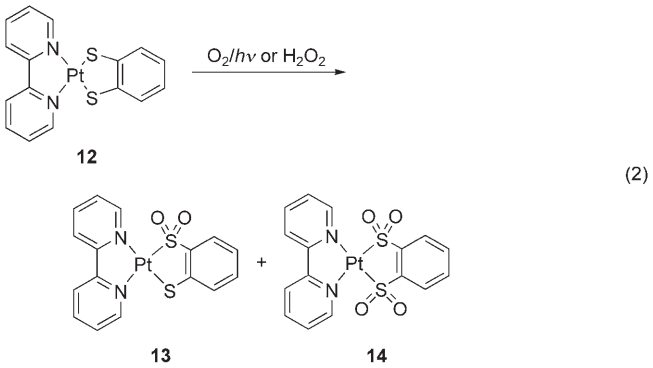



**a**: X = Y = S; **b**: X = S; Y = SO; **c**: X = S; Y = $SO_2$; **d**: X = SO; Y = $SO_2$; **e**: X = Y = $SO_2$

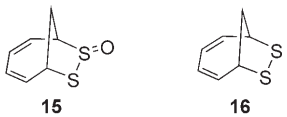
actions of (dithiolato)$Pt^{II}$ complexes have hardly been investigated so far in contrast to (dithiolato)$M^{II}$ complexes (M = Ni and Pd) of the same Group X elements which have been investigated in detail[16–27] in relation to the air sensitivity of transition-metal thiolates.[16]

Recently we reported that the reaction of cycloheptatriene with $S_8O$ gave bicyclic thiosulfinate **15**.[28] Compound



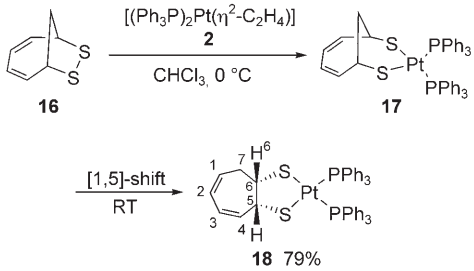

(2)

**15** was reduced with Lawesson's reagent to give bicyclic disulfide **16** as an orange oil, which polymerized within a few hours. The instability of **16** is ascribed to the large strain of the disulfide bond. The S–S bond length and the C-S-S-C dihedral angle were calculated to be 2.105 Å and 26.0°, respectively, at the B3LYP/6-311+G(3df) level of theory.[29] The value of the dihedral angle shows the large deviation from 90° of unstrained disulfides.[30] In this paper we report the reaction of this strained disulfide **16** with $Pt^0$ complex **2** in which we observed a unique rearrangement caused by the characteristic bicyclic ring system and we discuss the oxidation of the resulting (dithiolato)platinum(II) complex.




## Results and Discussion

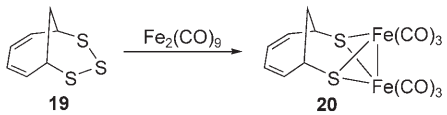
The reaction of disulfide **16** with $Pt^0$ complex **2** was carried out in $CHCl_3$ at 0 °C. The $^{31}P$ NMR spectrum of the reaction mixture exhibited a singlet at $\delta = 22.0$ ppm with satellite signals due to the isotope $^{195}Pt$ ($^1J(^{195}Pt,^{31}P) = 2936$ Hz), indicating the formation of a compound having a mirror plane. We assigned the structure of this compound to the expected (dithiolato)platinum(II) complex **17**. However, complex **17** was thermally unstable and gradually isomerized at room temperature to another (dithiolato)platinum(II) complex **18** [Eq. (3)]. The $^{31}P$ NMR spectrum of compound **18** exhibited two doublets at $\delta = 20.6$ and 21.7 ppm ($^2J(^{31}P,^{31}P) = 24$ Hz) accompanied by satellite signals due to the $^{195}Pt$ isotope ($^1J(^{195}Pt,^{31}P) = 2863$ and 2929 Hz). The $^1H$ NMR spectrum comprises signals due to four nonequivalent olefinic protons together with four nonequivalent aliphatic protons of the seven-membered ring. The multiplet ($\delta = 2.97$–$3.10$ ppm) accompanying the satellite signals due to the $^{195}Pt$ isotope ($^3J(^{195}Pt,H) = 36$ Hz) was assigned to the 6-H atom (see the Experimental Section).




(3)

The structure of **18** was unambiguously determined by X-ray crystallography (Figure 1, see also Figure 4) to be a (cyclohepta-1,3-diene-*cis*-5,6-dithiolato)$Pt^{II}$ complex. The cycloheptadiene ring was disordered in the crystal phase 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) and C(1B)-C(2B)-C(3)-C(4B)-C(5B)-C(6)-C(7B) rings, respectively, in which C(3) and C(6) were common.

Complex **18** is formed by a [1,5]-sulfur shift in **17**, unprecedented as far as we know, and the *cis* stereochemistry of the two sulfur atoms in **17** is retained. Shaver et al. reported that the reaction of trisulfide **19** with $[Fe_2(CO)_9]$ gives the corresponding diiron complex **20** [Eq. (4)], which decomposed in DMSO at around 120 °C.[31] On the other hand, Lorenz and co-workers reported the synthesis of **22** by photoreaction of **21** with cycloheptatriene.[32] The diiron complexes **20** and **22** correspond to the $Pt^{II}$ complexes **17** and **18**, respectively, but mutual isomerization between **20** and **22** was not reported.

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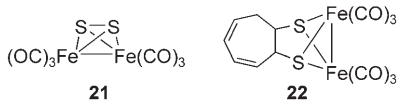


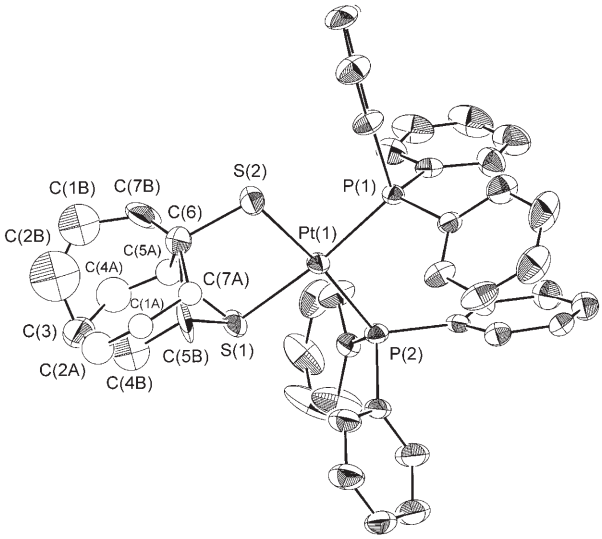




Figure 1. ORTEP drawing of (cyclohepta-1,3-diene-*cis*-5,6-dithiolato)platinum(II) complex **18** (at the 20% ellipsoidal probability level). The cycloheptadiene ring is disordered (see also Figure 4). C(1A), C(1B), C(2A), C(2B), C(4A), C(4B), C(5A), and C(7A) were refined isotropically. Hydrogen atoms and a solvate molecule ($CH_2Cl_2$) have been omitted for clarity.

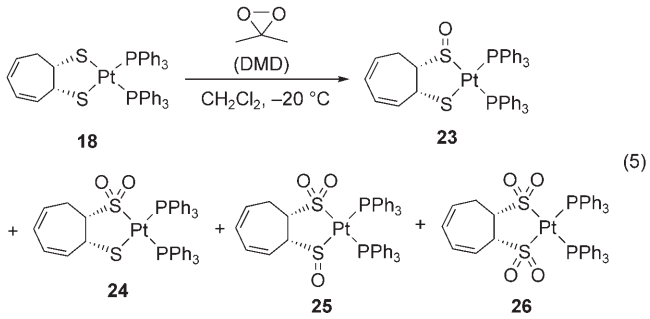
**Oxidation of (dithiolato)platinum(II) complex 18**: The regio- and stereoselectivities of the oxidation reactions of **18** were investigated. The oxidation reaction was expected to yield a maximum number of four isomeric monoxides up to the tetraoxide of **18**. Table 1 summarizes the results of the oxidation reactions performed with 1–4 equivalents of dimethyldioxirane (DMD) as the oxidizing reagent. The products obtained were (sulfenato-thiolato)platinum(II) complex **23**, (sulfinato-thiolato)platinum(II) complex **24**, (sulfenato-sulfinato)platinum(II) complex **25**, and (disulfinato)platinum(II) complex **26** [Eq. (5)].

Table 1. Yields of the oxidation products **23**–**26** and **18** based on the $^{31}P$ NMR integral ratio.[a]

| Run | DMD [equiv] | **23** [%] | **24** [%] | **25** [%] | **26** [%] | **18** [%] |
|---|---|---|---|---|---|---|
| 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) | – |

[a] Yields of isolated products are given in parentheses.

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

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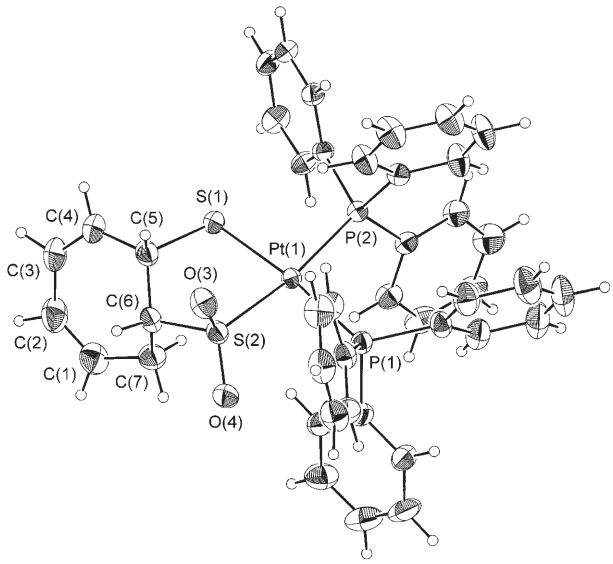



Figure 2. ORTEP drawing of (sulfinato-thiolato)platinum(II) complex **24** (30% ellipsoidal probability).

The other two products, 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 $^{31}P$ NMR data and the relevant reactions described later. Table 2 summarizes the $^{31}P$ NMR data of **18** and **23**–**26**. One of the two $^1J(^{195}Pt,^{31}P)$ coupling constants of **23** (2398 Hz) was much smaller than the other (3057 Hz), the latter being comparable to those of (dithiolato)platinum(II) complex **18** (2863 and 2929 Hz). The sets of $^1J(^{195}Pt,^{31}P)$ coupling constants of representative (sulfenato-thiolato)platinum(II) complexes **3**, **9b**, and **11b** are reported to be 2281 and 3201 Hz,[2] 2451 and 3587 Hz,[11] and 2295 and 3542 Hz,[12] respectively. Thus, the set of coupling constants (2398 and 3057 Hz) for **23** is consistent with the presence of a sulfenato substituent that has a stronger *trans* influence than the thiolato substituents.[2–12] 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**.

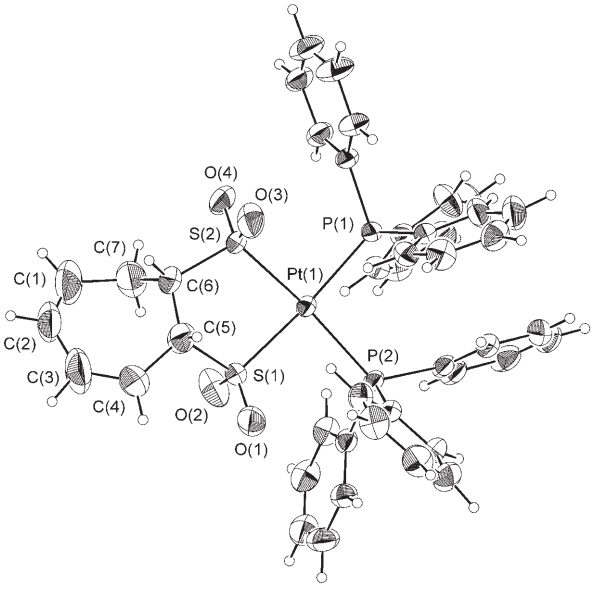
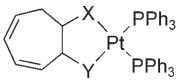



Figure 3. ORTEP drawing of (disulfinato)platinum(II) complex **26** (30% ellipsoidal probability).

Table 2. $^{31}$P NMR data for **18** and oxidation products **23**–**26**.

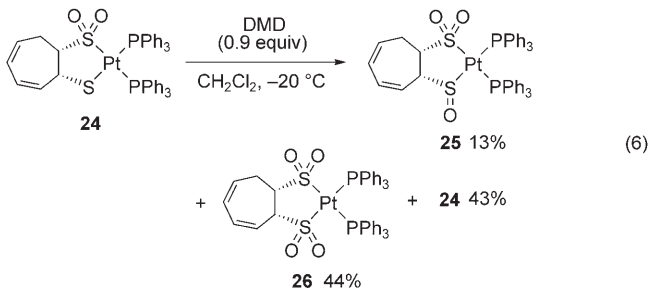



| | X,Y | $\delta$ [ppm] ($^1J(^{195}Pt,^{31}P)$ [Hz]) | $^2J(^{31}P,^{31}P)$ [Hz] |
|---|---|---|---|
| **18** | S,S | 20.6 (2863), 21.7 (2929) | 24 |
| **23** | SO,S | 16.9 (2398), 17.8 (3057) | 29 |
| **24** | $SO_2$,S | 13.8 (2554), 18.9 (3045) | 25 |
| **25** | $SO_2$,SO | 11.3 (2881), 14.9 (2404) | 27 |
| **26** | $SO_2$,$SO_2$ | 12.5 (2662), 13.8 (2764) | 22 |

The stereochemistry of the S=O group in **23** is not clear at present.

In the case of trioxide **25**, the signals centered at $\delta =$ 11.3 ppm have a $^1J(^{195}Pt,^{31}P)$ coupling constant of 2881 Hz assignable to the $^{31}$P atom *trans* to the -$SO_2$- group, though this value is larger by 117–327 Hz than those of **24** (2554 Hz) and **26** (2662 and 2764 Hz). The other $^{31}$P atom *trans* to the sulfenato substituent has a $^1J(^{195}Pt,^{31}P)$ coupling constant value of 2404 Hz, 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%) [Eq. (6)].

In the oxidation reaction of (dithiolato)platinum(II) complex **18** with DMD, the formation of neither another monoxide **27** nor *S*,*S*′-dioxide **28** was observed, indicating that the first oxidation reaction took place regioselectively and the second occurred exclusively at the sulfenato sulfur atom of **23**. The regioselectivity of the first step is discussed later in this paper. Reactivity similar to that of **23** has been reported for thiolate-type complexes by Schenk et al. [33] In the oxidation of [$CpRuL_2(SR)$] (Cp = cyclopentadienyl; $L_2 = 2PPh_3$, dppe, or $CO/PPh_3$; R = Me, Ph, or $PhCH_2$) with DMD, the initial oxidation product [$CpRuL_2${S(O)R}] underwent the second oxidation reaction much faster than the starting complex and the only detectable product was [$CpRuL_2(SO_2R)$], even when 1 mol equivalent of DMD was employed. Schenk et al. proposed that transition-metal sulfenates might be expected to be very good nucleophiles if the excellent π-donating ability of low-valent transition-metal fragments was taken into account,[33] which is true for the present case.

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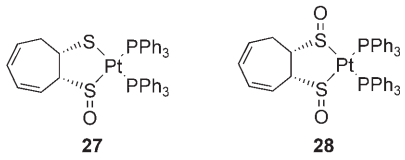



**Crystal structures of 18, 24, and 26**: The relevant bond lengths, bond angles, and dihedral angles of **18**, **24**, and **26** are summarized in Table 3. The Pt(1)−S(1) and Pt(1)−S(2) bond lengths are not influenced significantly by the oxidation state of the sulfur atoms and lie in the narrow range of 2.2990(15)–2.339(4) Å. The lengths of the Pt−P bonds *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)−P(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.[1–7,11,12] The S−O bond lengths are all similar.

**Regioselectivity of the oxidation of 18**: Complex **18** was oxidized with DMD at the sulfur atom assigned as S(2) in Figure 1. This regioselectivity cannot be attributed to electronic effects, but to steric effects around the sulfur atoms S(1) and S(2): The two sulfur atoms in **18** are considered to have a similar electronic nature because both of the phosphine ligands are *trans* and therefore exert the same effect on the sulfur atoms. In addition, it is hard to measure the difference between the inductive effects exerted by the allylic substituent on S(1) and the homo-allylic substituent on S(2).

Although the dithiaplatinabicyclo[5.3.0]decadiene ring moiety of **18** was disordered in the crystalline state, as de-

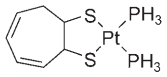
  

Table 3. Relevant bond lengths [Å], bond angles [°], and dihedral angles [°] of **18**, **24**, and **26**.

| | **18**[a] | **24** | **26** |
|---|---|---|---|
| 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 for **18** are mean values of two disordered structures. [b] Because of the disorder of the cycloheptadiene ring in **18**, the values have been excluded from discussion.

picted in Figure 1, we can divide the moiety into two components (Figure 4). The two $C_2S_2Pt$ five-membered rings, C(5A)-S(1)-Pt(1)-S(2)-C(6) (Figure 4a) and C(5B)-S(1)-Pt(1)-S(2)-C(6) (Figure 4b), adopt a distorted envelope conformation with C(5A) and 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 $C_2S_2Pt$ ring in tetraoxide **26** adopts an envelope conformation in which the C(5) is at the flap position and the S(1)-Pt(1)-S(2)-C(6) dihedral angle is 0.2(3)°, whereas in **24** the ring adopts a slightly distorted envelope conformation with the C(6) at the flap position and a S(2)-Pt(1)-S(1)-C(5) dihedral angle of 4.2(2)°. 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 baseline 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** adopts a conformation similar to that of **26**. DFT calculations[29] were carried out on model compound **29** employing the two different envelope conformations of **24** and **26** as the initial structures.[34] The two calculations gave the same optimized structure, which is very similar to that of **18** (Figure 5).



**29**

As shown in Figure 6, DMD approaches the sulfur atoms from directions axial to the five-membered ring. The approach of DMD from the *endo* side of the seven-membered ring with respect to the S(1) and S(2) atoms is substantially hindered by the axial $CH_2$ group bound to C(6). The axial hydrogen atom at C(5) disturbs the attack of DMD at the neighboring S(1) atom from the *exo* side of the seven-membered ring. Thus, the most 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 basis, the stereochemistry of the S=O group in **23** is *exo* to the cycloheptadiene ring. In the second oxidation reaction, monoxide **23** may change conformation and, more importantly, the electronic effect mentioned above allows DMD to attack S(2) again to give **24**. In **24**, the sulfur atom that undergoes oxidation [S(1)] is located on the baseline of the envelope conformation in a position favorable for the approach of DMD, as discussed above.

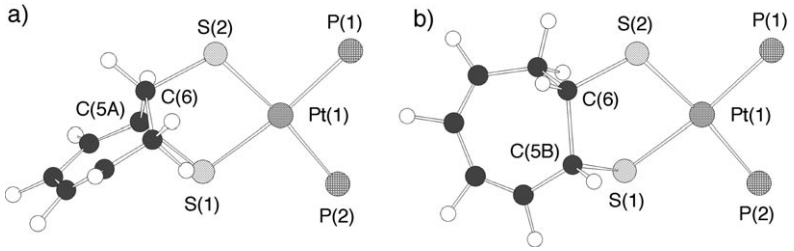



Figure 4. Two components of **18** in the crystalline state (phenyl groups have been omitted for clarity) (S(1)-Pt(1)-S(2)-C(6) 11.8(6)°).

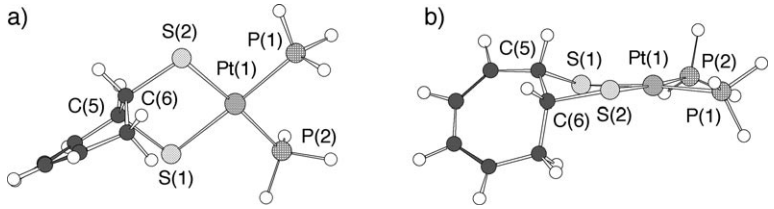



Figure 5. The optimized structure of **29** as determined by DFT calculations: a) Top view; b) side view; S(1)-Pt(1)-S(2)-C(6) 9.5°. Other relevant bond lengths [Å] and angles [°]: Pt(1)–S(1) 2.400, Pt(1)–S(2) 2.405, Pt(1)–P(1) 2.402, Pt(1)–P(2) 2.396, S(1)–C(5) 1.951, S(2)–C(6) 1.929, C(1)–C(2) 1.351, C(2)–C(3) 1.461, C(3)–C(4) 1.353, C(4)–C(5) 1.496, C(5)–C(6) 1.524, C(6)–C(7) 1.538; S(1)-Pt(1)-S(2) 88.6, S(2)-Pt(1)-P(1) 86.4, P(1)-Pt(1)-P(2) 98.7, P(2)-Pt(1)-S(1) 86.4, P(1)-Pt(1)-S(1) 174.0, P(2)-Pt(1)-S(2) 174.0, C(4)-C(5)-C(6)-C(7) 58.3.

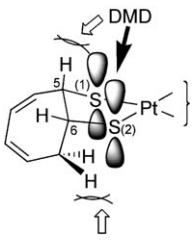



Figure 6. Attack of DMD on the sulfur atoms of **18** (**29**) from axial directions.

## Conclusion

We have found that the reaction of bicyclic disulfide **16** with $[(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)]$ (**2**) yielded the corresponding (dithiolato)-platinum(II) complex **17** by oxidative addition and that **17** isomerized to another (dithiolato)-platinum(II) complex **18** at room temperature by a [1,5]-sulfur rearrangement in the cycloheptadiene ring. The oxidation of **18** with DMD was investigated in detail. The reaction furnished (sulfenato-thiolato)platinum(II) **23**, (sulfinato-thiolato)platinum(II) **24**, (sulfenato-sulfinato)platinum(II) **25**, and (disulfinato)platinum(II) **26** complexes. The structures of **24** and **26** were determined unambiguously by X-ray crystallography. Through this technique we observed that the $C_2S_2Pt$ five-membered rings existed in two different envelope forms. Complex **18** was oxidized to monoxide **23** regioselectively, which can be explained in terms of a steric effect on the basis of the structure obtained by X-ray crystallography and DFT calculations. Complex **23** was oxidized not at the thiolato sulfur atom, but at the sulfenato sulfur atom to give *S*,*S*-dioxide **24**.

## Experimental Section

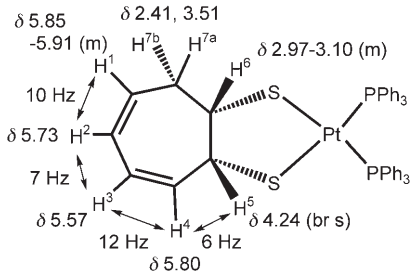
**General**: The melting points were determined in a Mel-Temp capillary tube apparatus and are uncorrected. $^1H$ and $^{31}P$ NMR spectra were determined on a Bruker AM400 or DRX400 (400 and 162 MHz, respectively) spectrometer using $CDCl_3$ as the solvent at 25 °C, unless otherwise noted. IR spectra were recorded with a Perkin-Elmer System 2000 FT-IR spectrometer. Elemental analyses were performed with a FISONS EA1108 by the Molecular Analysis and Life Science Center of Saitama University. Column chromatography was performed on 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 (Sigma-Aldrich).[35]

**Reaction of disulfide 16 with $[(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)]$ (2)**: A solution of disulfide **16** (11.0 mg, 0.0704 mmol) in chloroform (2 mL) was added to a solution of $[(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)]$ (**2**) (51.8 mg, 0.0693 mmol) in chloroform (3 mL) under argon at 0 °C over 5 min. The mixture was stirred for 15 min at 0 °C and the solvent was removed under reduced pressure. The $^1H$ and $^{31}P$ NMR spectra of the residue showed the formation of (dithiolato)$Pt^{II}$ complex **17**. The complex **17** was not obtained in pure form by column chromatography ($R_f$ = 0.25, $CH_2Cl_2$/$Et_2O$, 5:1).

**(Cyclohepta-1,3-diene-*cis*-5,7-dithiolato)bis(triphenylphosphine)platinum (17)**: $^1H$ 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 ppm (m, 30H); $^{31}P$ NMR: $\delta$ = 22.0 ppm [s, $^1J(^{195}Pt,^{31}P)$ = 2936 Hz].

**Isomerization of 17 to (dithiolato)platinum(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/diethyl ether, 5:1) to give **18** ($R_f$ = 0.4; 47.8 mg, 79 %).

**(Cyclohepta-1,3-diene-*cis*-5,6-dithiolato)bis(triphenylphosphine)platinum (18)**: Pale yellow crystals, m.p. 224–226 °C (decomp) (hexane/$CH_2Cl_2$). $^1H$ NMR: $\delta$ = 2.41 (pseudo dd, $J$ = 16.2, 8.5 Hz, 1H; 7a-H or 7b-H), 2.97–3.10 (m, $^3J(^{195}Pt,H)$ = 36 Hz, 1H; 6-H), 3.51 (pseudo dd, $J$ = 14.6, 12.4 Hz, 1H; 7a-H or 7b-H), 4.24 (br s, 1H; 5-H), 5.57 (dd, $J$ = 11.8, 6.9 Hz, 1H; 3-H), 5.73 (ddd, $J$ = 10.4, 7.3, 2.8 Hz, 1H; 2-H), 5.80 (dd, $J$ = 11.7, 5.7 Hz, 1H; 4-H), 5.85–5.91 (m, 1H; 1-H), 7.12–7.16 (m, 12H), 7.24–7.29 (m, 6H), 7.40–7.52 ppm (m, 12H); $^{31}P$ NMR: $\delta$ = 20.6 (d, $^2J(^{31}P,^{31}P)$ = 24 Hz, $^1J(^{195}Pt,^{31}P)$ = 2863 Hz), 21.7 ppm (d, $^2J(^{31}P,^{31}P)$ = 24 Hz, $^1J(^{195}Pt,^{31}P)$ = 2929 Hz); elemental analysis calcd (%) for $C_{43}H_{38}P_2PtS_2$: C 58.96, H 4.37; found: C 58.66, H 4.35. The assignment of the $^1H$ NMR data is based on a H-H COSY NMR experiment. Data for the seven-membered ring in **18** are summarized below.




**Oxidation of (dithiolato)platinum(II) complex 18 with DMD**

**With one equivalent 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 °C under argon. After stirring for 2 h at this temperature, the solvent was removed under reduced pressure at −20 °C. The $^{31}P$ NMR spectrum of the residue showed the formation of (sulfenato-thiolato)platinum(II) complex **23** (10 %), (sulfinato-thiolato)platinum(II) complex **24** (11 %), (sulfenato-sulfinato)-platinum(II) complex **25** (8 %), (disulfinato)platinum(II) complex **26** (4 %), and **18** (67 %).

**With two equivalents 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 °C. The $^{31}P$ NMR spectrum of the reaction mixture showed the formation of (sulfenato-thiolato)platinum(II) complex **23** (16 %), (sulfinato-thiolato)platinum(II) complex **24** (28 %), (sulfenato-sulfinato)platinum(II) complex **25** (17 %), (disulfinato)platinum(II) complex **26** (16 %), and **18** (23 %). The mixture was subjected to column chromatography (dichloromethane/diethyl 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.

**With three equivalents 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 °C. The $^{31}P$ NMR spectrum of the reaction mixture showed the formation of (sulfinato-thiolato)platinum(II) complex **24** (30 %), (sulfenato-sulfinato)platinum(II) complex **25** (43 %), (disulfinato)platinum(II) complex **26** (21 %), and **18** (6 %). The mixture was subjected to column chromatography (dichloromethane/diethyl ether, 4:1) to give **24** (5 mg, 22 %) and **26** (4.8 mg, 21 %). Complex **25** decomposed in the column.

**With 3.5 equivalents 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 $^{31}P$ NMR spectrum of the reaction mixture showed the formation of (sulfenato-sulfinato)platinum(II) complex **25** (47 %) and (disulfinato)platinum(II) complex **26** (53 %).

**With four equivalents 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 $^{31}P$ NMR spectrum of the reaction mixture showed the formation of only (disulfinato)platinum(II) complex **26** as the complex. The mixture was subjected to column chromatography (dichloromethane/diethyl ether, 4:1) to give **26** (21.2 mg, 87 %).

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

**(Cyclohepta-1,3-diene-*cis*-6-sulfinato-5-thiolato)bis(triphenylphosphine)-platinum (24)**: Orange crystals, m.p. 225–227 °C (decomp) (EtOH/$CH_2Cl_2$). $^1$H NMR: $\delta$ = 2.65–2.80 (m, $^3J(^{195}Pt,H)$ = 24 Hz, 1H), 2.85–2.92 (m, 1H), 2.98–3.05 (m, 1H), 4.19 (brs, 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 ppm (m, 12H); $^{31}$P NMR: $\delta$ = 13.8 (d, $^2J(^{31}P,^{31}P)$ = 25 Hz, $^1J(^{195}Pt,^{31}P)$ = 2554 Hz), 18.9 ppm (d, $^2J(^{31}P,^{31}P)$ = 25 Hz, $^1J(^{195}Pt,^{31}P)$ = 3045 Hz); IR (KBr): $\tilde{\nu}$ = 1206, 1052 cm$^{-1}$ ($SO_2$); elemental analysis calcd (%) for $C_{43}H_{38}O_2P_2PtS_2$: C 56.88, H 4.22; found: C 56.62, H 4.15.

**(Cyclohepta-1,3-diene-*cis*-5-sulfenato-6-sulfinato)bis(triphenylphosphine)platinum (25)**: $^1$H NMR: $\delta$ = 2.75–2.84 (m, 1H), 3.11–3.28 (m, $^3J(^{195}Pt,H)$ = 25 Hz, 1H), 3.75–3.85 (m, 1H), 3.87 (brs, 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 ppm; $^{31}$P NMR: $\delta$ = 11.3 (d, $^2J(^{31}P,^{31}P)$ = 27 Hz, $^1J(^{195}Pt,^{31}P)$ = 2881 Hz), 14.9 ppm (d, $^2J(^{31}P,^{31}P)$ = 27 Hz, $^1J(^{195}Pt,^{31}P)$ = 2404 Hz).

**(Cyclohepta-1,3-diene-*cis*-5,6-disulfinato)bis(triphenylphosphine)platinum (26)**: Pale yellow crystals, m.p. 176–179 °C (decomp) (EtOH/$CH_2Cl_2$). $^1$H NMR: $\delta$ = 2.08–2.12 (m, 1H), 2.80–2.86 (m, 1H), 3.06–3.14 (m, 1H), 4.34 (brs, 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 ppm (m, 6H); $^{31}$P NMR: $\delta$ = 12.5 (d, $^2J(^{31}P,^{31}P)$ = 22 Hz, $^1J(^{195}Pt,^{31}P)$ = 2662 Hz), 13.8 ppm (d, $^2J(^{31}P,^{31}P)$ = 22 Hz, $^1J(^{195}Pt,^{31}P)$ = 2764 Hz); IR (KBr): $\tilde{\nu}$ = 1225, 1052 cm$^{-1}$ ($SO_2$); elemental analysis calcd (%) for $C_{44}H_{40}Cl_2O_4P_2PtS_2$ ($C_{43}H_{38}O_4P_2PtS_2{\cdot}CH_2Cl_2$): C 51.57, H 3.93; found: C 51.84, H 3.89.

**X-ray crystallography**: A Mac Science DIP3000 diffractometer with a graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda$ = 0.71073 Å) was used. Data reduction was carried out using the maXus program.[36] Absorption corrections were performed using the multi-scan method (SORTAV[37]). The structure was solved by a direct method (SIR97[38] or DIRDIF96[39]) and refined by a full-matrix least-squares (SHELXL-97[40]) method 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**: $C_{43}H_{38}P_2PtS_2{\cdot}CH_2Cl_2$, $M_r$ = 960.87, yellow plates, 0.26 × 0.14 × 0.10 mm$^3$, monoclinic, $P2_1/c$, $a$ = 13.4020(10), $b$ = 9.8730(7), $c$ = 32.167(3) Å, $\beta$ = 109.249(18)°, $V$ = 4018.3(6) Å$^3$, $\rho_{calcd}$ = 1.448 g cm$^{-3}$, $Z$ = 4, $\mu(Mo_{K\alpha})$ = 3.840 cm$^{-1}$. Intensity data for 7875 unique reflections were collected in the range $-16 \le h \le 14$, $-11 \le k \le 11$, $-40 \le l \le 41$. $R_1$ = 0.0752 ($I > 2\sigma I$, 4285 reflections), $wR_2$ = 0.1879 (for all), and GOF = 1.044, 461 parameters; max/min residual electron density = 1.142/−0.970 e Å$^{-3}$. 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**: $C_{43}H_{38}O_2P_2PtS_2$, $M_r$ = 907.941, orange plates, 0.36 × 0.36 × 0.26 mm$^3$, monoclinic, $P2_1/c$, $a$ = 15.3910(4), $b$ = 13.1450(4), $c$ = 20.2431(9) Å, $\beta$ = 112.995(18)°, $V$ = 3770.1(2) Å$^3$, $\rho_{calcd}$ = 1.600 g cm$^{-3}$, $Z$ = 4, $\mu(Mo_{K\alpha})$ = 3.954 cm$^{-1}$. Intensity data for 7926 unique reflections were collected in the range $-19 \le h \le 19$, $-16 \le k \le 16$, $-24 \le l \le 25$. $R_1$ = 0.0397 ($I > 2\sigma I$, 7088 reflections), $wR_2$ = 0.1109 (for all), and GOF = 1.076, 452 parameters; max/min residual electron density = 2.648/−1.002 e Å$^{-3}$.

**Crystal data for 26**: $C_{43}H_{38}O_4P_2PtS_2$, $M_r$ = 939.94, pale yellow cubes, 0.18 × 0.16 × 0.12 mm$^3$, monoclinic, $P2_1/c$, $a$ = 12.7380(4), $b$ = 20.9550(7), $c$ = 16.9978(7) Å, $\beta$ = 123.561(1)°, $V$ = 3780.8(2) Å$^3$, $Z$ = 4, $\rho_{calcd}$ = 1.651 g cm$^{-3}$, $Z$ = 4, $\mu(Mo_{K\alpha})$ = 3.950 cm$^{-1}$. Intensity data for 7433 unique reflections were collected in the range $-16 \le h \le 16$, $-26 \le k \le 26$, $-17 \le l \le 18$. $R_1$ = 0.0439 ($I > 2\sigma I$, 6456 reflections), $wR_2$ = 0.1241 (for all), and GOF = 1.141, 470 parameters; max/min residual electron density = 1.212/−0.985 e Å$^{-3}$.

CCDC-628607 (**18**), CCDC-628608 (**24**), and CCDC-628609 (**26**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Oxidation of (sulfinato-thiolato)platinum(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 $^{31}$P NMR spectrum of the residue showed the formation of **25** and **26** and residual **24** in a ratio of 13:44:43.

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