

Oxosulfido Complexes of Platinum — $(\text{Ph}_3\text{P})_2\text{Pt}(\text{S}_2\text{O})$ and $(\text{Ph}_3\text{P})_4\text{Pt}_2(\mu\text{-S})(\mu\text{-SO})$ — Their Formation and Properties

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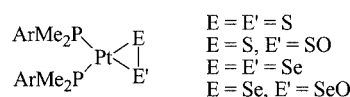
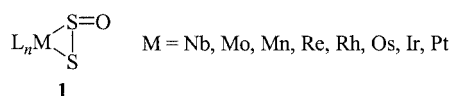
Keywords: Platinum / S ligands / Oxo ligands

The platinum S_2O complex $[(\text{Ph}_3\text{P})_2\text{Pt}(\text{S}_2\text{O})]$ (**10**) was obtained by S_2O transfer reactions from tetrathiolane 2-oxide (**8**), tetrathiolane 2,3-dioxide (**5**), and pentathiane 3-oxide (**6**) to $[(\text{C}_2\text{H}_4)\text{Pt}(\text{PPh}_3)_2]$ (**4**). The S_2O complex **10** further reacts

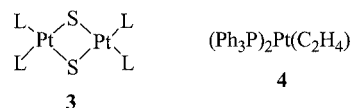
with **4** to give a novel binuclear platinum complex **16**, which is found to be a source of several platinum S_nO_m complexes. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2003)

The coordination chemistry of organotransition metal compounds of sulfur oxides has been attracting considerable attention.^[1–4] Among them, disulfur monoxide (S_2O) complexes **1** of several transition metals (Nb,^[5] Mo,^[6] Mn,^[7–11] Re,^[8] Rh,^[2] Os,^[12] Ir,^[2,5,9,10,12,13] and Pt^[14]) are known, in which platinum– S_2O complexes **2** ($\text{E} = \text{S}$, $\text{E}' = \text{SO}$) were reported very recently by Tokitoh and co-workers.^[14] They synthesized the platinum– S_2O and $-\text{Se}_2\text{O}$ complexes, **2** by oxidation of the respective S_2 and Se_2 complexes,^[15] which were prepared for the first time by taking advantage of bulky phosphane ligands (TbtMe_2P and BbtMe_2P). Similarly, most of the other S_2O complexes were synthesized by oxidation of the corresponding S_2 complexes, and a few were prepared by S_2O transfer reactions from 4,5-diphenyl-3,6-dihydro-1,2-dithiin 1-oxide^[6,9,10] or reaction with $\text{S}_2\text{O}(\text{THF})_x$.^[2] On the other hand, the chemistry of sulfido complexes of platinum bearing the Pt_2S_2 core (**3**) has also been drawing considerable interest.^[16] Another recent topic in this field is oxidative additions of Pt^0 complex **4** to a thiosulfate $[-\text{S}-\text{S}(\text{O})-]$ moiety in cyclic sulfur compounds.^[17–21] We have been studying the synthesis and reactivities of cyclic polysulfides, and have reported on the chemistry of tetrathiolane 2,3-dioxide (**5**),^[22,23] pentathiane 3-oxide (**6**),^[24,25] and S_8O ,^[26] all of which act as S_2O transfer reagents.^[27–30] Recently we also reported the reaction of dithiirane 1-oxides **7** with **4**.^[31] Here, we report the reaction of **5**, **6**, and tetrathiolane 2-oxide (**8**)^[23] with **4**, where an S_2O transfer took place giving rise to $[(\text{Ph}_3\text{P})_2\text{Pt}(\text{S}_2\text{O})]$

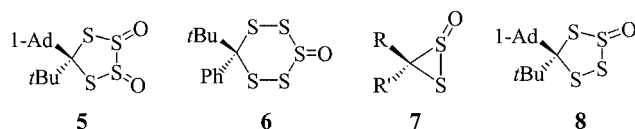
which further reacted with **4** to yield the binuclear platinum complex $[(\text{Ph}_3\text{P})_4\text{Pt}_2(\mu\text{-S})(\mu\text{-SO})]$.



Ar = 2,4,6-[(Me₃Si)₂CH]₃C₆H₂ (Tbt) or 2,6-[(Me₃Si)₂CH]₂-4-[(Me₃Si)₃C]C₆H₂ (Bbt)



L = phosphine ligands

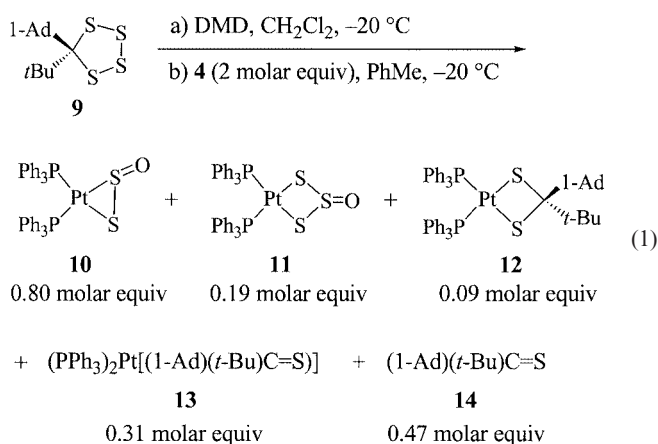


1-Ad = 1-adamantyl

Tetrathiolane 2-oxide (**8**), prepared in situ by oxidation of tetrathiolane (**9**) with dimethyldioxirane (DMD)^[32,33] at -20°C ,^[23] was allowed to react with two molar equivalents of **4** in toluene at -20°C to produce $[(\text{Ph}_3\text{P})_2\text{Pt}(\text{S}_2\text{O})]$ (**10**; 0.80 molar equiv.), $[(\text{Ph}_3\text{P})_2\text{Pt}(\text{S}_3\text{O})]$ (**11**; 0.19 molar equiv.),^[34] the dithiolato complex **12** (0.09 molar equiv.), $[(\text{Ph}_3\text{P})_2\text{Pt}\{(\text{1-Ad})(\text{tBu})\text{C}=\text{S}\}]$ (**13**; 0.31 molar equiv.),^[31] and $(\text{1-Ad})(\text{tBu})\text{C}=\text{S}$ (**14**; 0.47 molar equiv.) [Equation (1)].

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The structure of the S_2O complex **10** was determined by X-ray crystallography (Figure 1).^[35] The crystal contained one molecule of benzene — the recrystallization solvent — per two molecules of **10**, and the $\text{Pt}(\text{S}_2\text{O})$ moiety was disordered as shown in Figure 1a: the occupancies of the set A [$\text{Pt}(1\text{A})\text{S}(1\text{A})\text{S}(2\text{A})\text{O}(1\text{A})$] and the set B [$\text{Pt}(1\text{B})\text{S}(1\text{B})\text{S}(2\text{B})\text{O}(1\text{B})$] were almost equivalent (0.515 and 0.485, respectively). Figure 1b shows the whole of the molecule

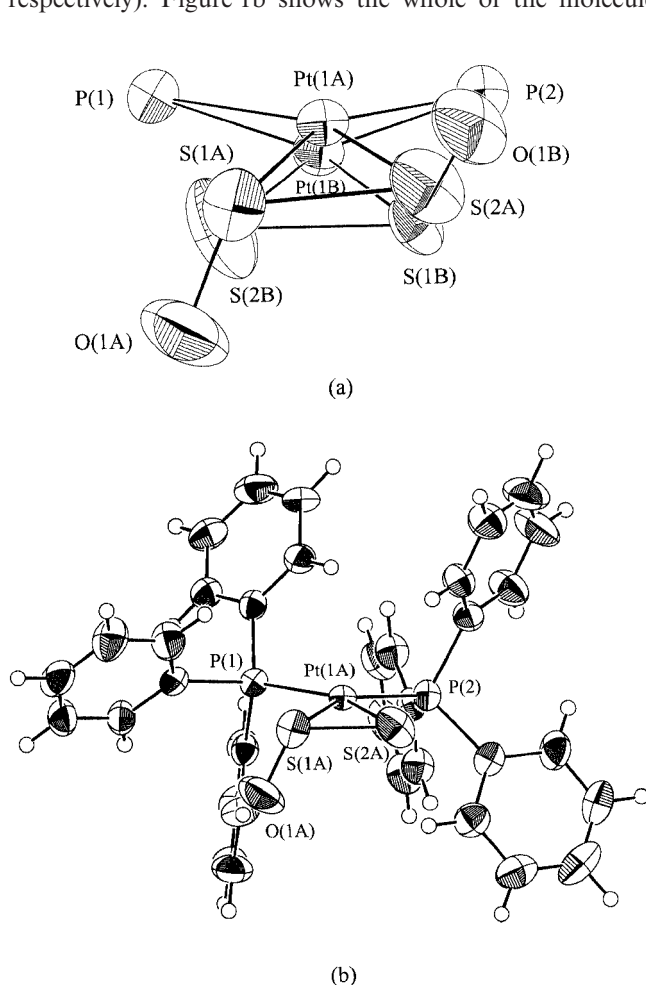
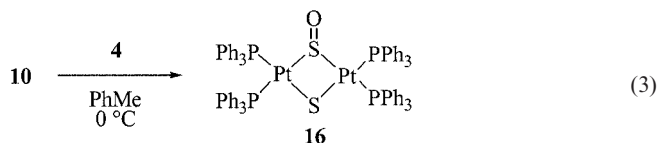
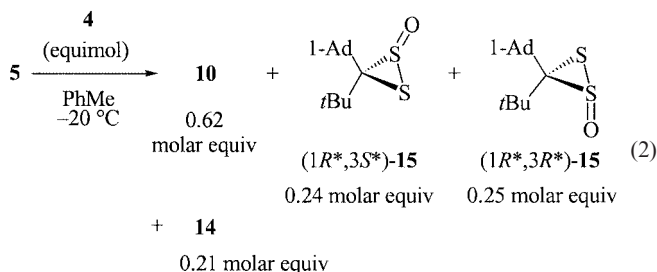


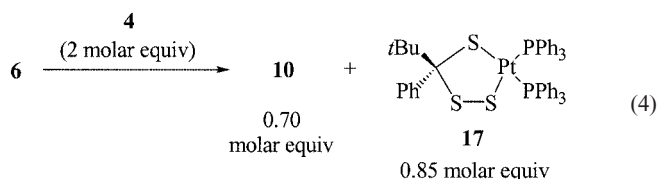
Figure 1. ORTEP drawings of $(\text{Ph}_3\text{P})_2\text{Pt}(\text{S}_2\text{O})$ (**10**) (50% ellipsoidal probability): (a) disorder of the $\text{Pt}(\text{S}_2\text{O})$ moiety (phenyl groups are omitted for clarity), set A (0.515 occupancy) $\text{Pt}(1\text{A})\text{S}(1\text{A})\text{S}(2\text{A})\text{O}(1\text{A})$, set B (0.485 occupancy) $\text{Pt}(1\text{B})\text{S}(1\text{B})\text{S}(2\text{B})\text{O}(1\text{B})$; (b) the whole of **10** drawn with the set A

with only the set A. In the ^{31}P NMR spectrum, two doublets appear at $\delta = 18.2$ and 18.4 [$^2J_{\text{P,P}} = 7$ Hz] with satellite signals due to the ^{195}Pt nucleus [$^1J_{\text{Pt,P}} = 4364$ and 3410 Hz in CDCl_3 , respectively]. These coupling constant values are quite similar to those of the S_2O complex **2** ($\text{Ar} = \text{Bbt}$, $\text{E} = \text{S}$, $\text{E}' = \text{SO}$) [$^2J_{\text{P,P}} = 8$, $^1J_{\text{Pt,P}} = 4263$ and 3254 Hz].^[14] Shaver reported that the S_3O complex **11** can be obtained by reaction of $[(\text{PPh}_3)_2\text{Pt}(\text{SH})_2]$ with SO_2 ,^[34] while we found that the reaction of S_8O with **4** yields **11** in good yield.^[36]

The reaction of tetrathiolane 2,3-dioxide (**5**) with an equimolar amount of **4** yielded the S_2O complex **10** (0.62 molar equiv.) along with $(1R^*,3S^*)$ - and $(1R^*,3R^*)$ -dithiirane 1-oxides (**15**)^[22,23] (0.24 and 0.25 molar equiv., respectively) and thioketone **14** (0.21 molar equiv.) [Equation (2)]. Interestingly, when two molar equivalents of **4** were employed, binuclear platinum complex **16** was obtained. Indeed, the isolated S_2O complex **10** reacted with **4** very quickly to give **16** in high yield [Equation (3)]. Insertion reactions of **4** into the S-S bond of cyclic oligosulfide oxides^[17–21] and $\text{Fe}_2(\mu\text{-S}_2)(\text{CO})_6$ ^[37] have been reported. The properties of complex **16** will be described later in this paper.



Similarly, pentathiane 3-oxide (**6**) was treated with **4** (2 molar equiv.) to furnish the S_2O complex **10** and the dithiolato-thiolato complex **17** in 0.70 and 0.85 molar equiv., respectively [Equation (4)]. The structure of **17** was determined by X-ray crystallography (Figure 2).^[35]



Interestingly, complex **17** decomposes in CDCl_3 at 65°C (2 h) to give an alternative complex **18** (0.23 molar equiv.) and t-Bu(Ph)C=S (0.23 molar equiv.) [Equation (5)]. Complex **18** exhibits a singlet at $\delta = 22.7$ ($^1J_{\text{Pt,P}} = 3939$ Hz) in the ^{31}P NMR spectrum of the mixture, and this $^1J_{\text{Pt,P}}$ value is quite similar to that of **2** ($\text{Ar} = \text{Bbt}$, $\text{E} = \text{E}' = \text{S}$) ($\delta = -32.2$ ppm, $^1J_{\text{Pt,P}} = 3909$ Hz).^[15] Thus, we tentatively as-

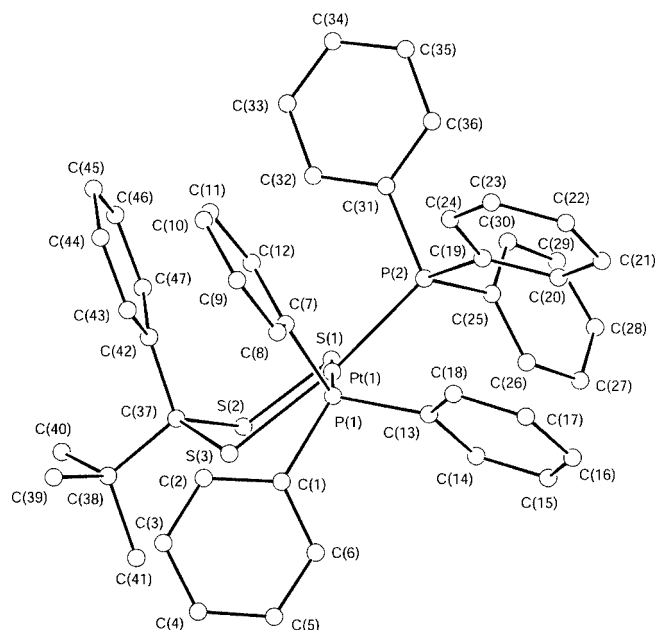
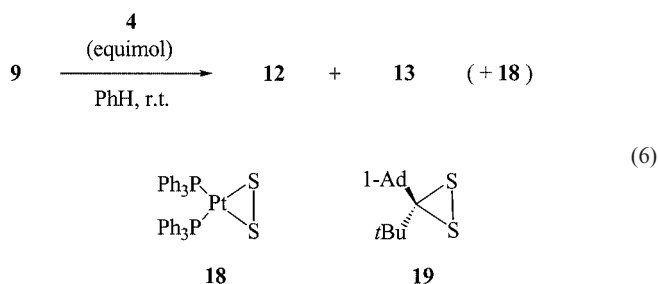
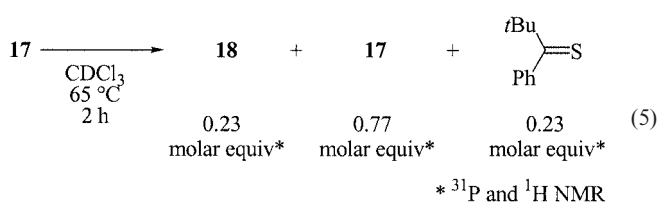
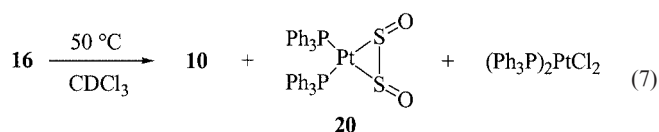


Figure 2. Molecular structure of $[(t\text{Bu})(\text{Ph})\text{CS}_3]\text{Pt}(\text{PPh}_3)_2$ (**17**); hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [deg]: Pt(1)–P(1) 2.2854(19), Pt(1)–P(2) 2.297(3), Pt(1)–S(3) 2.307(2), Pt(1)–S(1) 2.3350(18), S(1)–S(2) 2.061(4), S(2)–C(37) 1.837(9), S(3)–C(37) 1.837(8), P(1)–Pt(1)–P(2) 99.39(8), P(1)–Pt(1)–S(3) 86.99(8), P(2)–Pt(1)–S(3) 171.29(8), P(1)–Pt(1)–S(1) 174.65(9), P(2)–Pt(1)–S(1) 84.32(8), S(3)–Pt(1)–S(1) 89.74(8), S(2)–S(1)–Pt(1) 106.27(12), C(37)–S(2)–S(1) 100.5(3), C(37)–S(3)–Pt(1) 103.6(3), C(7)–P(1)–Pt(1) 114.7(3), C(13)–P(1)–Pt(1) 111.5(3), C(1)–P(1)–Pt(1) 115.4(3), C(31)–P(2)–Pt(1) 112.7(4), C(25)–P(2)–Pt(1) 112.4(3), C(19)–P(2)–Pt(1) 120.3(3), S(2)–C(37)–S(3) 105.3(5), C(42)–C(37)–C(38) 112.1(8)

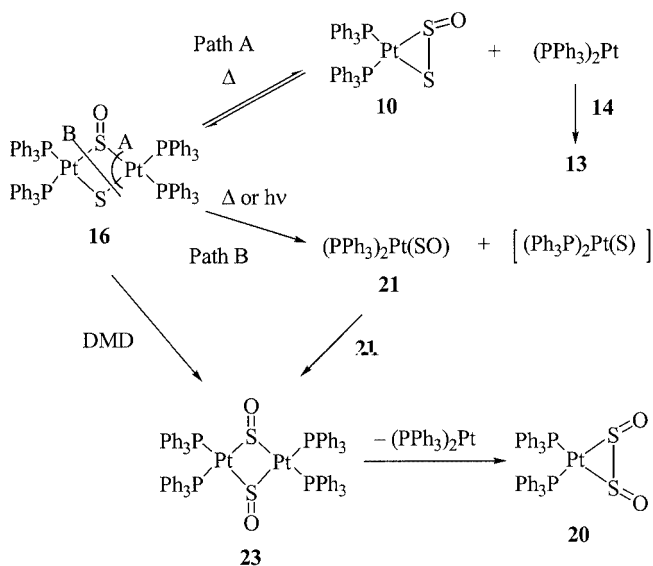
signed the S_2 complex structure **18** to this compound. However, the complex was not stable enough to be isolated; prolonged heating of the mixture or even allowing it to stand at room temperature for several hours led to complete disappearance of the signal. We also examined the reaction of tetrathiolane **9** with **4**. The reaction yielded mainly the dithiolato complex **12** and the thioketone complex **13**. In addition, ^{31}P NMR spectroscopy showed a small signal due to **18** [Equation (6)]. The dithiolato complex **12** was also formed by the reaction of dithiirane **19** with **4** in benzene.^[38]



We tried to prepare the binuclear platinum complex **16** by oxidation of $[(\text{Ph}_3\text{P})_2\text{Pt}]_2(\mu\text{-S})_2$ (**3**; $\text{L} = \text{PPh}_3$).^[39] It has been reported that oxidation of a binuclear platinum complex bridged by S gives the $\mu\text{-SO}$ complex.^[40] However, **16** was not obtained because of the insolubility of $[(\text{Ph}_3\text{P})_2\text{Pt}]_2(\mu\text{-S})_2$ in the usual organic solvents. Complex **16** decomposes upon heating at 50°C in CDCl_3 to yield the S_2O complex **10**, the S_2O_2 complex **20**,^[41] and $[(\text{PPh}_3)_2\text{PtCl}_2]$ [Equation (7)]. The identification of the S_2O_2 complex **20** was done by comparison of the ^{31}P NMR spectrum of an authentic sample prepared by the reported method.^[41] The decomposition in the presence of (1-Ad)(*t*Bu)C=S (**14**) in PhH yielded the thioketone complex **13** and the S_2O complex **10** as the main products in 0.66 and 0.61 molar equiv., respectively, along with the S_2O_2 complex **20** and recovered thioketone **14**. The formation of the thioketone complex **13** indicates the intervention of $(\text{PPh}_3)_2\text{Pt}$.

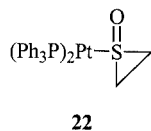


A plausible mechanism for the thermal decomposition of **16** is depicted in Scheme 1. Initially, **16** decomposes via two pathways: in Path A, it extrudes $(\text{PPh}_3)_2\text{Pt}$, which is trapped by thioketone **14** to yield **13**, to give the S_2O complex **10**; in Path B, **16** splits into the SO complex **21** and $[(\text{PPh}_3)_2\text{Pt}(\text{S})]$. Lorenz and Kull have reported that an attempt to prepare the SO complex **21** by thermolysis of the episulfide complex **22** results in the formation of the S_2O_2 complex **20**.^[41] We propose that the SO complex **21** dimerizes to give another binuclear platinum complex **23** that readily extrudes $(\text{PPh}_3)_2\text{Pt}$ to furnish the S_2O_2 complex **20**. This proposal is strongly supported by the fact that oxidation of **16** with



Scheme 1. Plausible mechanism for reactions of the platinum dinuclear complex **16**

DMD yields the S_2O_2 complex **20** in high yield, probably via **23**. The fate of $[(PPh_3)_2Pt(S)]$ is unclear, but the formation of $[(PPh_3)_2PtCl_2]$ upon thermolysis in $CDCl_3$ implies the formation of $[(Ph_3P)_2Pt(\mu-S)_2]$ (**3**; $L = PPh_3$), which reportedly reacts with CH_2Cl_2 to give $[(PPh_3)_2PtCl_2]$.^[16] Irradiation of **16** with light in $CDCl_3$ gave the S_2O_2 complex **20**, $[PtCl_2(PPh_3)_2]$, and $Ph_3P=X$ ($X = O, S$) indicating that Path B is dominant in the photolysis.



In summary, the platinum S_2O complex **10** was obtained by S_2O transfer reactions from tetrathiolane 2-oxide (**8**), tetrathiolane 2,3-dioxide (**5**) and pentathiane 3-oxide (**6**) to $[(PPh_3)_2Pt(C_2H_4)]$ (**4**). The S_2O complex **10** further reacts with **4** to give a novel binuclear platinum complex **16**, which is found to be a source of several platinum- S_nO_m complexes.

Experimental Section

Reaction of Tetrathiolane 2-Oxide (8) with 4: An acetone solution of DMD (0.106 m, 0.30 mL, 0.032 mmol) was added to a solution of tetrathiolane **9** (10 mg, 0.031 mmol) in CH_2Cl_2 (2 mL) at $-20^\circ C$ under argon. The mixture was stirred for 1 h at this temperature and then the solvent was removed in vacuo below $-20^\circ C$. The residue was dissolved in toluene (1 mL) at $-20^\circ C$ and then treated with a solution of $[(PPh_3)_2Pt(C_2H_4)]$ (**4**; 48 mg, 0.062 mmol) in toluene (2 mL). After stirring for 10 min, the solvent was evaporated to dryness and the residue was subjected to column chromatography (silica gel, CH_2Cl_2/Et_2O , 5:1) to elute first a mixture of 1-adamantyl *tert*-butyl thioketone (**14**), the dithiolato complex (**12**), and $[(PPh_3)_2Pt\{(1-Ad)(tBu)C=S\}]$ (**13**) and then $[(PPh_3)_2Pt(S_2O)]$ (**11**; 4.9 mg, 0.19 molar equiv.) and $[(PPh_3)_2Pt(S_2O)]$ (**10**; 19.7 mg, 0.80 molar equiv.) in this order. The mixture of **12**, **13**, and **14** was further subjected to gel permeation chromatography (GPC) with $CHCl_3$ as solvent to give a mixture (12.8 mg) of **12** (0.09 molar equiv.) and **13** (0.31 molar equiv.), and 1-adamantyl *tert*-butyl thioketone (**14**; 3.5 mg, 0.47 molar equiv.). The yields of **12** and **13** were estimated on the basis of the 1H NMR integral ratio. The crude S_2O complex **10** was precipitated from a mixed solvent of dichloromethane and hexane, and the collected powder was washed with benzene several times to give the analytical sample. When the reaction was conducted using four molar equivalents of **4**, the thioketone complex **13** was not formed and the dithiolato complex **12** was isolated in nearly pure form after chromatographic purification. The crude dithiolato complex **12** was washed with ethanol several times to give the analytical sample.

10: Yellow powder, m.p. $200^\circ C$ (dec.). 1H NMR (400 MHz, $CDCl_3$): $\delta = 7.15-7.23$ (m, 12 H), $7.28-7.36$ (m, 18 H) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 18.2$ (d, $^2J_{Pt,P} = 7$, $^1J_{Pt,P} = 4364$ Hz), 18.4 (d, $^2J_{Pt,P} = 7$, $^1J_{Pt,P} = 3409$ Hz) ppm. FAB MS (*m*-nitrobenzyl alcohol): $m/z = 800$ [$M^+ + 1$], 719. $C_{36}H_{30}OP_2PtS_2$ (799.78): calcd. C 54.06, H 3.78; found C 53.58, H 3.54.

12: Off-white powder, m.p. $225-226^\circ C$ (dec.). 1H NMR (400 MHz, $CDCl_3$): $\delta = 1.20-1.40$ (m, 9 H), $1.52-1.68$ (m, 6 H), 1.94 (br. s, 3 H), 2.21 (br. s, 6 H), 7.14 (t, $J = 7.0$ Hz, 12 H),

7.23 (t, $J = 7.0$ Hz, 6 H), $7.44-7.49$ (m, 12 H) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 22.9$ (s, $^1J_{Pt,P} = 2925$ Hz) ppm. FAB MS (*m*-nitrobenzyl alcohol): $m/z = 989$ [$M^+ + 1$], 931, 853. $C_{51}H_{54}P_2PtS_2$ (988.14): calcd. C 61.99, H 5.51; found C 62.00, H 5.62.

Reaction of Tetrathiolane 2,3-Dioxide 5 with 4

Equimolar Amount of 4: Compound **4** (20.7 mg, 0.0277 mmol) was added to a solution of **5** (10.1 mg, 0.0277 mmol) in toluene (1 mL) at $-20^\circ C$ under argon. The mixture was stirred for 1 h at this temperature and the solvent was then evaporated to dryness. The residue was subjected to column chromatography (silica gel, CH_2Cl_2/Et_2O , 5:1) to give a mixture of thioketone **14** and the $(1R^*,3R^*)$ - and $(1R^*,3S^*)$ -dithiirane 1-oxides **15**, and the S_2O complex **10** (13.8 mg, 0.62 molar equiv.). The mixture of **14** and **15** was further subjected to HPLC (silica gel, CH_2Cl_2 /hexane 1:1) to give the thioketone **14** (1.4 mg, 0.21 molar equiv.), $(1R^*,3R^*)$ -dithiirane 1-oxide [$(1R^*,3R^*)$ -**15**; 1.9 mg, 0.24 molar equiv.], and $(1R^*,3S^*)$ -dithiirane 1-oxide [$(1R^*,3S^*)$ -**15**; 2.0 mg, 0.25 molar equiv.].

Two Molar Equivalents of 4: Tetrathiolane **9** (10 mg, 0.031 mmol) was oxidized with four molar equivalents of DMD (0.102 m, 1.2 mL, 0.123 mmol) in dichloromethane (1.5 mL) for 1 h at $-20^\circ C$. The solvent was removed under reduced pressure below $-20^\circ C$, and the resulting tetrathiolane 2,3-dioxide **5** was used without further purification. The 2,3-dioxide **5** was dissolved in toluene (2 mL) at $-20^\circ C$, and the solution was treated with a solution of **4** (45 mg, 0.060 mmol) in toluene (2 mL) at this temperature. The solution turned immediately from colorless to deep yellow and was stirred for 10 min at $-20^\circ C$. Removal of the solvent under reduced pressure gave an orange residue, the ^{31}P NMR integral ratio of which indicated the formation of the thioketone complex **13**, $[(PPh_3)_4Pt_2-(\mu-S)(\mu-SO)]$ (**16**), the S_2O complex **10**, and the S -oxides of **12**^[31] in the molar ratio of 26:13:29:32, along with $Ph_3P=O$ and $Ph_3P=S$. The molar ratio was obtained based on the ^{31}P NMR integral ratio. The S -oxides of **12** are considered to be formed by reactions of dithiirane 1-oxides **15** with **4**.^[31] The binuclear platinum complex **16** could not be isolated in this experiment because it was not eluted from the silica-gel column.

Reaction of the S_2O Complex 10 with 4: A solution of **4** (21.7 mg, 0.029 mmol) in toluene (1.5 mL) was added at $0^\circ C$ to a solution of **10** (23.2 mg, 0.029 mmol) in toluene (1.5 mL) under argon. The mixture was stirred for 1 h at $0^\circ C$, and the solution was concentrated to ca. one-fourth of its original volume under reduced pressure. Diethyl ether was added to precipitate the product, and the resulting precipitates were collected by filtration to give 47.7 mg (0.71 molar equiv.) of $[(PPh_3)_4Pt_2(\mu-S)(\mu-SO)]$ (**16**).

16: Yellow powder, m.p. $179^\circ C$ (dec.). 1H NMR (400 MHz, $CDCl_3$): $\delta = 6.97-7.02$ (m, 24 H), $7.11-7.18$ (m, 12 H), $7.29-7.34$ (m, 12 H), $7.47-7.52$ (m, 12 H) ppm. ^{31}P NMR ($CDCl_3$, 162 MHz): $\delta = 21.0$ (m, $^1J_{Pt,P} = 3394$ Hz), 21.8 (m, $^1J_{Pt,P} = 2427$ Hz) ppm. IR (KBr): $\tilde{\nu} = 1095$ cm^{-1} . ESI MS: $m/z = 1519.2$ [$M^+ + 1$]. $C_{72}H_{60}OP_4Pt_2S_2$ (1519.44): calcd. C 56.91, H 3.98; found C 56.13, H 3.94.

Reaction of Pentathiane 3-Oxide 6 with 4: A solution of **4** (84 mg, 0.113 mmol) in toluene (12 mL) was added over 15 min to a solution of **6** (18 mg, 0.056 mmol) in toluene (2 mL) at $-15^\circ C$. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography (silica gel, $CHCl_3$ and then CH_2Cl_2/Et_2O 4:1) to give $[(tBu)(Ph)CS_3]Pt(PPh_3)_2$ (**17**; 46 mg, 0.85 molar equiv.) and the S_2O complex **10** (31.3 mg, 0.70 molar equiv.). **17:** Yellow crystals, m.p. $143-147^\circ C$ (dec.) ($CHCl_3/EtOH$). 1H NMR ($CDCl_3$, 400 MHz): $\delta = 1.11$ (s, 9 H), $6.95-7.01$ (m, 6 H),

7.03–7.09 (m, 6 H), 7.14–7.19 (m, 8 H), 7.26–7.38 (m, 7 H), 7.48–7.54 (m, 6 H), 8.08–8.11 (m, 2 H) ppm. ^{31}P NMR (162 MHz, CDCl_3): δ = 18.5 (d, $^2J_{\text{P,P}} = 23$, $^1J_{\text{Pt,P}} = 2754$ Hz), 22.9 (d, $^2J_{\text{P,P}} = 23$, $^1J_{\text{Pt,P}} = 3057$ Hz) ppm. $\text{C}_{47}\text{H}_{44}\text{P}_2\text{PtS}_3 \cdot 2\text{CHCl}_3$ ($\text{C}_{49}\text{H}_{46}\text{Cl}_6\text{P}_2\text{PtS}_3$; 1200.80): calcd. C 49.01, H 3.86; found C 49.06, H 3.75.

Reaction of Tetrathiolane 9 with 4: Compound 4 (6.1 mg, 0.0081 mmol) was added at room temperature to a solution of 9 (2.7 mg, 0.0081 mmol) in benzene (2 mL). The yellow mixture was stirred for 15 min at room temperature, and the solvent was removed under reduced pressure. The ^{31}P NMR spectrum of the residue indicated the formation of the dithiolato complex 12, the thioketone complex 13, and a compound assigned tentatively to the S_2 complex 18 (δ = 22.7 ppm, $^1J_{\text{Pt,P}} = 3939$ Hz) in the molar ratio of 32:57:11.

Thermal Decomposition of 16. In CDCl_3 : A solution of 16 (10 mg, 0.0065 mmol) in CDCl_3 (4 mL) under argon was heated at 50 °C for 1.5 h. The ^{31}P NMR spectrum of an aliquot taken from the mixture indicated the formation of the S_2O complex 10, the S_2O_2 complex 20 (δ = 6.4, $^1J_{\text{Pt,P}} = 4019$ Hz), $[(\text{PPh}_3)_2\text{PtCl}_2]$ (δ = 14.9, $^1J_{\text{Pt,P}} = 3672$ Hz), 16, $\text{Ph}_3\text{P}=\text{S}$ (δ = 44.0 ppm), and $\text{Ph}_3\text{P}=\text{O}$ (δ = 29.8 ppm) in the molar ratio of 33:11:21:11:14:11.

In Benzene in the Presence of Thioketone 14: A solution of 16 (23 mg, 0.015 mmol) and 14 (3.6 mg, 0.015 mmol) in benzene (4.5 mL) was heated at 50 °C for 4 h under argon, and then the solvent was removed under reduced pressure. The ^{31}P NMR spectrum of the residue indicated the formation of the thioketone complex 13, the S_2O complex 10, and the S_2O_2 complex 20 in the molar ratio of 50:43:7. The residue was subjected to column chromatography (silica gel, $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$, 5:1) to give a mixture of 14 and 13 (14 mg), and 10 (7.4 mg, 0.61 molar equiv.). The S_2O_2 complex 20 was not eluted from the silica-gel column. The molar ratio of 14 and 13 was 31:69, giving calculated yields of 0.0042 mmol (0.28 molar equiv.) and 0.010 mmol (0.66 molar equiv.), respectively.

When a solution of 16 (10 mg, 0.0065 mmol) in benzene (1.5 mL) was heated at 50 °C, 1.0 mg of unidentifiable precipitates (ESI-MS: m/z = 999.5) were collected by filtration.

Photolysis of 16: A solution of 16 in CDCl_3 in an NMR tube was irradiated with a high-pressure Hg lamp through a Pyrex filter in an ice-water bath for 1 h. The ^{31}P NMR spectrum showed the formation of the S_2O_2 complex 20, $[(\text{PPh}_3)_2\text{PtCl}_2]$, $\text{Ph}_3\text{P}=\text{O}$, and $\text{Ph}_3\text{P}=\text{S}$ in the molar ratio of 19:24:40:16. The signals due to the S_2O complex 10 were not observed (it was verified by a controlled experiment that 10 barely decomposed under the conditions).

Acknowledgments

We are grateful to Dr. Hideki Saito (Saitama University) for kind discussion on the X-ray analysis of 10. This work was supported by a Grant-in-Aid for Scientific Research (No. 12440174) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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[35] Crystal data for 10: $\text{C}_{36}\text{H}_{30}\text{OP}_2\text{PtS}_2 \cdot 0.5\text{C}_6\text{H}_6$ ($\text{C}_{39}\text{H}_{33}\text{OP}_2\text{PtS}_2$), M_w = 838.858, yellow plate, $0.30 \times 0.16 \times 0.06$ mm³, monoclinic, space group $P2_1/c$, a = 9.6861(6), b = 21.5760(10), c = 20.540(2) Å, β = 126.779(9)°, V = 3438.1(4) Å³, Z = 4, $\rho_{\text{calcd.}}$ = 1.621 g cm⁻³, $\mu(\text{Mo-K}\alpha)$ = 4.326 mm⁻¹. Intensity data of 7920 independent reflections were collected in the range of $-12 \leq h \leq 12$, $0 \leq k \leq 28$, $-26 \leq l \leq 12$ with a Mac Science MXC18 diffractometer using graphite-monochromated Mo- K_α radiation (λ = 0.71073 Å) at 298 K. The structure was solved by direct methods using SIR^[42] and refined with full-matrix least-squares (SHELXL-97^[43]) using all the independent reflec-

tions for 442 parameters. Absorption corrections were done by a psi-scan method. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed at calculated positions. Final $R1 = 0.0608$ [$I > 2\sigma(I)$, 6880 reflections], $wR2 = 0.1465$ (for all), $GOF = 1.315$; max/min residual density = $1.584/-2.129 \text{ e} \cdot \text{\AA}^{-3}$. Selected bond lengths [\AA] and angles [deg]: Pt(1A)–S(1A) 2.34(2), Pt(1A)–S(2A) 2.362(18), Pt(1A)–P(1) 2.286(6), Pt(1A)–P(2) 2.267(6), S(1A)–O(1A) 1.50(3), S(1A)–S(2A) 2.09(3), S(1A)–Pt(1A)–S(2A) 52.7(6), P(1)–Pt(1A)–S(1A) 102.0(5), P(2)–Pt(1A)–S(2A) 102.5(5), P(1)–Pt(1A)–P(2) 102.0(2), P(2)–Pt(1A)–S(1A) 153.4(5), P(1)–Pt(1A)–S(2A) 154.6(5), Pt(1B)–S(1B) 2.292(17), Pt(1B)–S(2B) 2.30(3), Pt(1B)–P(1) 2.270(7), Pt(1B)–P(2) 2.320(6), S(1B)–O(1B) 1.456(17), S(1B)–S(2B) 2.09(3), S(1B)–Pt(1B)–S(2B) 54.1(7), P(1)–Pt(1B)–S(1B) 155.2(4), P(2)–Pt(1B)–S(2B) 157.9(7), P(1)–Pt(1B)–P(2) 100.9(3), P(2)–Pt(1B)–S(1B) 103.8(4), P(1)–Pt(1B)–S(2B) 101.2(7). Crystal data for **17**: $\text{C}_{47}\text{H}_{44}\text{P}_2\text{PtS}_3 \cdot 2\text{CHCl}_3$ ($\text{C}_{49}\text{H}_{46}\text{Cl}_6\text{P}_2\text{PtS}_3$), $M_w = 1200.855$, yellow plate, $0.18 \times 0.12 \times 0.06 \text{ mm}^3$, monoclinic, space group $P2_1/n$, $a = 15.0340(9)$, $b = 20.890(2)$, $c = 16.1150(10) \text{ \AA}$, $\beta = 98.270(3)^\circ$, $V = 5008.5(6) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd.}} = 1.593 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 3.344 \text{ mm}^{-1}$. 9865 independent reflections were collected in the range of $-19 \leq h \leq 16$, $0 \leq k \leq 26$, $0 \leq l \leq 20$ with a Mac Science DIP3000 diffractometer using graphite-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 298 K. Absorption corrections were done by a multi-scan method (SORTAV^[44]). 581 parameters,

$R1 = 0.0606$ [$I > 2\sigma(I)$, 4874 reflections], $wR2 = 0.1212$ (for all), $GOF = 0.888$; max/min residual density = $0.807/-0.708 \text{ e} \cdot \text{\AA}^{-3}$.

CCDC-212018 (**10**) and CCDC-212019 (**17**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (internat.) +44-1223/336-033; or deposit@ccdc.cam.ac.uk).

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Received June 6, 2003