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Oxidation of Spirocyclohexyl-1,2,4-trithiolane and Complexation Reaction with $[Pt(\eta^2\text{-nb})(PPh_3)_2]$

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Oxidation of spirocylcohexyl-1,2,4-trithiolane **1** yielded the 4-*S*- and 1-*S*-oxide, **2** and **3**, respectively. The complexation reactions of **1**–**3** with $[Pt(\eta^2\text{-nb})(PPh_3)_2]$ (**4**; nb = norbornene) have been studied. The formed dithiolato, thioketone, thiolatosulfenato and sulfine complexes **5**–**8** have been isolated and characterized by ^{1}H-, ^{31}P NMR and IR spectroscopy and by mass spectrometry. The mechanism of the reaction is discussed. The reaction proceeds by insertion of the Pt^0 complex fragment into the sulfur–sulfur bond and subsequent ring contraction by extrusion of a thioketone or sulfine. Comparison of the molecular structures of the oxidized complexes **7** and **8** with the nonoxidized complex **5** shows elongation of the sulfenato–platinum bond and elongation of the platinum–phosphorus bond in the corresponding *trans* position. The product formed suggests that, in this system, formation of thiolato–platinum bonds is energetically favoured to sulfenato–platinum bonds. The structures of **5**, **7** and **8** were established by X-ray crystallography.

Introduction

1,2,4-Trithiolanes form a class of sulfur-rich five-membered heterocycles, which have attracted considerable attention in recent times. The parent compound as well as some 3,5-dialkyl-1,2,4-trithiolanes are naturally occurring substances.[1] On the other hand, 3,3,5,5-tetrasubstituted derivatives are easily formed as interception products of the reaction of intermediate thiocarbonyl *S*-sulfides (thiosulfines) with dipolarophilic thioketones.[2]

It is well known that the heating of these heterocycles in solution or in the gas phase (Flash Vacuum Pyrolysis, FVP) results in a cycloreversion reaction leading to thiosulfines (existing in an equilibrium with isomeric dithiiranes) and the corresponding thioketones.[3,4] In this way, 1,2,4-trithiolanes are used as a convenient source of in situ formed thiosulfines, which subsequently can be trapped by other dipolarophiles.[4] Very recently 1,2,4-trithiolanes have been used for syntheses of mimics for the active site of [Fe-only]-hydrogenase.[5,6] Along with the parent 1,2,4-trithiolane, there are also some oxidized species found in marine organisms.[7] In a recent investigation, the parent as well as the 3,3,5,5-tetramethyl-1,2,4-trithiolane were oxidized, and the diverse oxides were obtained and characterized. The study showed that the oxidation reactions with *m*-chloroperbenzoic acid (*m*-CPBA) result in the formation of a mixture of 1-*S*- and 4-*S*-oxides in comparable amounts.[8] Over the last years, reactions of cyclic disulfanes, thiosulfinates and thiosulfonates with Pt^0 have been described, which result in dithiolato, sulfenato thiolato, sulfinato thiolato, as well as thiosulfonato Pt^{II} complexes. Except for the latter compound, all the compounds were formed by oxidative addition of Pt^0 complexes to the S–S(O)$_n$ moiety (n = 0–2).[9–13] 1,2,4-Trithiolanes and their 1-*S*-oxides undergo reactions with Pt^0 complexes.[9,13]

Here we present a systematic investigation of the reactivity of the 1,2,4-trithiolane **1** and of its 4-*S*- and 1-*S*-oxide, **2** and **3**, respectively, with $[Pt(\eta^2\text{-nb})(PPh_3)_2]$ (**4**; nb = norbornene).

Results and Discussion

The spirocyclohexyl-1,2,4-trithiolane **1** was oxidized by using *m*-CPBA. After separation by means of column chromatography, two main products were obtained as pure compounds (Scheme 1), along with some starting material and a mixture of two higher oxides.[14] The ^{13}C NMR spectrum of the first eluted fraction shows 12 different signals. The signals at δ = 95.5 and 82.3 ppm are assigned to the quaternary C atoms C3 and C5. The second eluted fraction shows only six different signals, and for C3 and C5, only one signal at δ = 84.6 ppm is found. The elemental analysis and the found molecular peak in the mass spectra confirm

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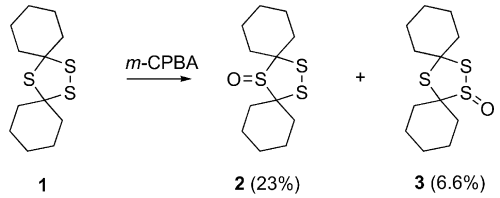
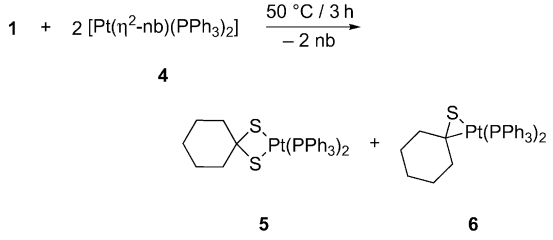
the formula $C_{12}H_{20}S_3O$; hence, the minor product is the 1-*S*-oxide **3** and the major product must be the 4-*S*-oxide **2**. The amount of the isolated 4-*S*-oxide **2** is nearly four times that of the 1-*S*-oxide **3**. Both products are crystalline; they are therefore more manageable than the tetramethyl derivatives.[8] The tendency to form the 4-*S*-oxide over the 1-*S*-oxide is well known for the unsubstituted 1,2,4-trithiolane and 3,3,5,5-tetramethyl-1,2,4-trithiolane.[7,8] In contrast, for the more bulkily substituted derivatives, such as tetraphenyl[13] and 3,5-di-*tert*-butyl-3,5-diphenyl derivatives,[15] exclusive oxidation at S1 and S2 is observed.



Scheme 1. Oxidation of spirocyclohexyl-1,2,4-trithiolane **1**.

Treatment of spirocyclohexyl-1,2,4-trithiolane **1** with 2 equiv. [Pt(η²-nb)(PPh_3)$_2$] (**4**) in toluene at 50 °C yielded a 1:1 mixture of two complexes (Scheme 2) in the crude product according to the ^{31}P NMR spectrum. This spectrum showed the existence of two spin systems, one A_2 spin system with a ^1J(P,Pt) value of 2971 Hz and an AB spin system with a ^2J(P,P) value of 16 Hz and ^1J(P,Pt) values of 4600 Hz and 2838 Hz. The first spin system is typical for complexes of the type [Pt(PPh_3)$_2$(S_2CR_2)] and is assigned to the dithiolato complex **5**; fractional crystallization gave the pure complex **5** in 64% yield with respect to 2 equiv. **4**. The results of the X-ray analysis are shown in Figure 1. The complex has a distorted quadratic planar geometry with a small S–Pt–S angle of 75.54(2) °. The S–Pt bond lengths of 2.3123(7) and 2.3231(7) Å are slightly longer than the P–Pt bond lengths of 2.2874(7) and 2.2820(6) Å. The structure is comparable to those reported for the similar complexes.[10,16]



Scheme 2. Reaction of 1,2,4-trithiolane **1** with platinum complex **4**.

The second spin system observed in the ^{31}P NMR spectrum is assigned to the thioketone complex **6**. An independent synthesis from cyclohexanonethione and [Pt(η²-nb)(PPh_3)$_2$] yielded a sample whose identity was confirmed to be **6** by TLC and ^{31}P NMR spectroscopy. The fragmentation of **1** found is similar to that reported for the reaction of bulkily substituted 1,2,4-trithiolanes with $Fe_2(CO)_9$.[5]

Similar treatment of the 4-*S*-oxide **2** with excess [Pt(η²-nb)(PPh_3)$_2$] gave a 1:1 mixture of the thioketone complex **6**

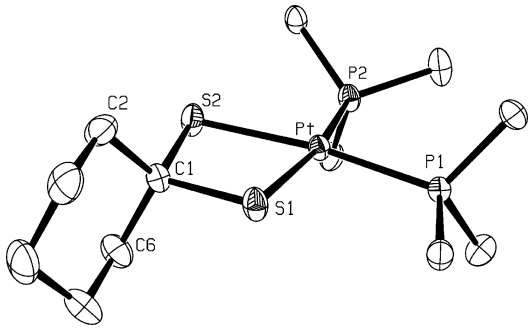
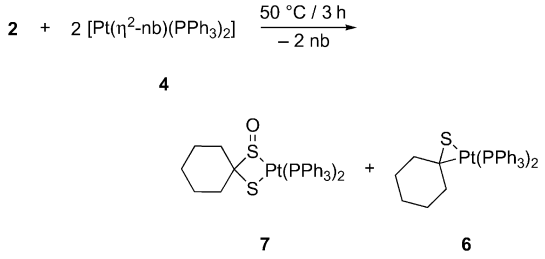


Figure 1. ORTEP[26] drawing of the molecular structure of the dithiolato complex **5** (for clarity, hydrogen atoms are omitted and the phenyl groups are represented only by their *ipso*-carbon atoms). Selected bond lengths (Å) and angles (°): Pt–P2 2.2874(7); Pt–P1 2.2820(6); Pt–S1 2.3123(7); Pt–S2 2.3231(7); S1–C1 1.847(3); S2–C1 1.836(3); P2–Pt–P1 99.89(2); S1–Pt–S2 75.54(2).

and a second complex **7** (Scheme 3). The pure complex **7** was isolated in 52% yield with respect to 2 equiv. **4** in a manner similar to that described for the dithiolato complex **5**. The ^{31}P NMR spectrum of **7** shows an AB spin system with a ^2J(P,P) value of 16 Hz and ^1J(P,Pt) values of 3324 Hz and 2343 Hz. Elemental analysis and mass spectroscopy confirm the molecular formula of $C_{42}H_{40}OP_2PtS_2$. In the IR spectrum, a strong broad band is found at $\tilde{\nu}$ = 995 cm^{-1}, which is typical for sulfenato ligands bound to platinum(II).[11d,13] Finally, X-ray analysis unambiguously confirms the expected structure of the sulfenato thiolato complex **7**. The molecular structure of **7** is shown in Figure 2.



Scheme 3. Reaction of spirocyclohexyl-1,2,4-trithiolane 4-*S* oxide **2** with **4**.

The complex has a distorted sqare–planar geometry. The sulfur–platinum bond length (S1–Pt) is 2.3174(6) Å and is in the range of those found in the dithiolato complex **5**. A similar bond length relative to that in **5** is observed for the phosphorus–platinum bond P2–Pt [2.2944(6) Å] in the *trans* position. In contrast, the sulfur–platinum bond S2–Pt to the sulfenato ligand is slightly elongated by 0.01 Å. The higher *trans* influence of the sulfenato ligand results in an elongation the P1–Pt bond by approximately 0.04 Å. This observation is in a good agreement with the smaller value observed for the ^1J(P,Pt) constant. The sulfur–oxygen bond in the sulfenato ligand [1.503(2) Å] is slightly longer than those reported for similar sterically crowded complexes.[12]

Complex **4** reacted with the 1-*S* oxide **3** at room temperature in a few minutes to yield a 1:1 mixture of the dithiolato complex **5** and a new product **8**, which shows an AB spin system with a ^2J(P,P) value of 24 Hz and ^1J(P,Pt) values of

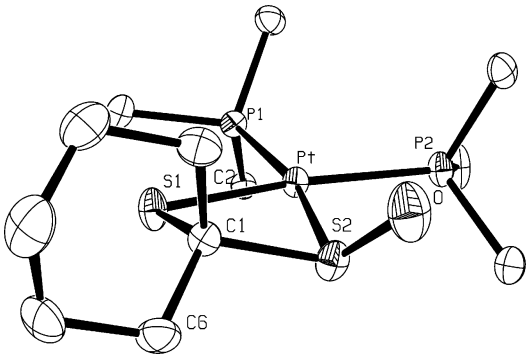


Figure 2. ORTEP[26] drawing of the molecular structure of the sulfenato thiolato complex **7** (for clarity, hydrogen atoms are omitted and the phenyl groups are represented only by their *ipso*-carbon atoms). Selected bond lengths (Å) and angles (°): Pt–P2 2.2944(6); Pt–P1 2.3193(6); Pt–S1 2.3174(6); Pt–S2 2.3336(6); S1–C1 1.837(2); S2–C1 1.858(2); S2–O 1.503(2); P2–Pt–P1 100.01(2); S1–Pt–S2 74.33(2).

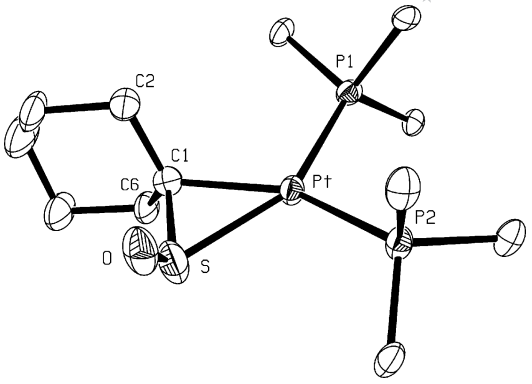
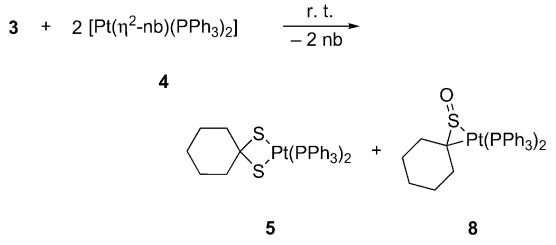


Figure 3. ORTEP[26] drawing of the molecular structure of the sulfine complex **8** [for clarity, hydrogen atoms and O1A are omitted and the phenyl groups are represented only by their *ipso*-carbon atoms]. Selected bond lengths (Å) and angles (°): Pt–P2 2.3038(16); Pt–P1 2.2867(16); Pt–S1 2.3338(18); Pt–C1 2.126(6); S1–C1 1.770(6); S1–O1 1.436(8); S1–O1A 1.321(13); P2–Pt–P1 105.29(6); S1–Pt–C1 46.48(17).

3817 Hz and 3075 Hz in the ^{31}P NMR spectrum (Scheme 4). In the mass spectrum, the molecular peak is found at m/z = 850, and the elemental analysis confirms the molecular formula $C_{42}H_{40}OP_2PtS$. On the basis of these data, structure **8** can be assigned to the isolated complex. The result is in good agreement with that observed in the reaction between 3,3,5,5-tetraphenyl-1,2,4-trithiolane 1-*S*-oxide and $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$.[13] Recrystallization from a thf/pentane mixture yielded crystals that were suitable for X-ray analysis. The results are shown in Figure 3.



Scheme 4. Reaction of spirocyclohexyl-1,2,4-trithiolane 1-*S* oxide **3** with **4**.

The sulfine fragment incorporated in complex **8** is coordinated by an η^2 mode and the complex has a distorted square-planar coordination sphere. The structure is comparable with that reported for the 9*H*-fluorene-9-thione-*S*-oxide complex.[17] The P1–Pt bond located in the *trans* position to the oxidized sulfur atom has a length of 2.2867(16) Å and the value for this bond length falls at the higher end of the range (2.25–2.30 Å) found for thioketone complexes.[9,10,18,19] In contrast to that found in the structure of **6**, the sulfur–platinum bond in **8** is remarkably longer [2.3338(18) Å] than those found in thioketone complexes (2.27–2.29 Å).[9,10,18,19] In the registered spectra of the crude product, there is no indication for the formation of **6** or **7**.

Taking this into account, the reactions of 1,2,4-trithiolane **1** and of the oxides **2** and **3** likely proceed in the first step by insertion of the Pt^0 complex fragment into the sulfur–sulfur bond of the 1,2,4-trithiolane ring.[9,11b,13] Ring contraction of the six-membered platinacycles formed, by expulsion of a thioketone or sulfine, leads to the four-membered platinacycles **5** and **7**, respectively. The former thioether sulfur atom is bonded to the platinum atom. In the last step, the thioketone or sulfine is complexed by a second equivalent of **4** to yield **6** or **8**, respectively. The exclusive formation of **5** and **8** in the reaction of the 1-*S*-oxide **3** with **4** suggests the favoured formation of thiolato ligands instead of sulfenato ligands in this system.

Conclusions

In summary, the reactions of spirocylcohexyl-1,2,4-trithiolane **1** and of its 4-*S*- and 1-*S*-oxide, **2** and **3**, respectively, proceed by insertion of the Pt^0 complex fragment into the sulfur–sulfur bond and subsequent ring contraction by expulsion of a thioketone or sulfine. The reactions yield the thioketone complex **6** and dithiolato complex **5**, as well as their mono *S*-oxides **8** and **7**. Comparison of the molecular structures of the oxidized and nonoxidized complexes shows an elongation of the sulfenato–platinum bond as well as the elongation of the platinum–phosphorus bond in the corresponding *trans* position. Selective extrusion of a sulfine instead of the thioketone in the case of **3** suggests that the formation of thiolato–platinum bonds is energetically favoured over sulfenato–platinum bonds.

Experimental Section

General: Melting points were determined with an AXIOLAB microscope with a TMHS 600 heating plate and are uncorrected. ^1H-, ^{31}P- and ^{13}C NMR spectra were determined with BRUKER DRX 400 or BRUKER DRX 200 spectrometers at 30 °C; chemical shifts are referred to the protons of the solvent or 85% H_3PO_4. ^{31}P- and ^{13}C NMR spectra are proton decoupled. IR spectra were recorded with a PERKIN ELMER System 2000 FT-IR spectrome-

ter. Mass spectra were recorded with a FINNIGAN MAT SSQ 710 mass spectrometer. Elemental analyses were determined with a LECO CHNS-932. All reactions were performed under argon, and solvents were dried by using sodium/benzophenone. Starting materials 7,14,15-trithia-dispiro[5.1.5.2]pentadecane (**1**)[20] and the Pt^0 complex **4**[18] were prepared according to the literature procedures.

Oxidation of Spirocyclohexyl-1,2,4-trithiolane 1: *m*-CPBA (70%, 1.2 g, 5.4 mmol) dissolved in CH_2Cl_2 (10 mL) was added in small portions to a solution of spirocyclohexyl-1,2,4-trithiolane **1** (1 g, 3.8 mmol) in CH_2Cl_2 (20 mL) at 0 °C. The reaction mixture was stirred for an additional 2 h and subsequently washed with a diluted aqueous solution of $NaHCO_3$. The organic layer was separated, dried with Na_2SO_4, and reduced to dryness, and the residue was subjected to column chromatography to yield the 1-*S*-oxide **3** and the 4-*S*-oxide **2**, as well as a mixture of higher oxides.

Spirocyclohexyl-1,2,4-trithiolane 1-*S*-Oxide 3: Colourless crystals. Yield: 70 mg (6.6%). M.p. 46 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.25–2.1 (m, 4 H), 2.1–1.9 (m, 4 H), 1.8–1.3 (m, 12 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 95.5 (q-C), 82.3 (q-C), 49.5, 43.6, 36.8, 32.4, 26.8, 26.1, 25.6, 25.0, 24.2, 23 ppm. IR (KBr): $\tilde{\nu}$ = 2920 (s), 1447 (s), 1098 [s, (S=O)] cm^{-1}. $C_{12}H_{20}OS_3$ (277.49): calcd. C 52.13, H 7.29, S 34.79; found C 52.15, H 6.59, S 35.01.

Spirocyclohexyl-1,2,4-trithiolane 4-*S*-Oxide 2: Colourless crystals. Yield: 240 mg (23%). M.p. 115 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.09 (m), 1.90 (dt), 1.78 (m), 1.63 (m), 1.33 (m) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 84.6 (q-C), 33.7, 28.2, 25.2, 24.6, 23.1 ppm. IR (KBr): $\tilde{\nu}$ = 2931 (s), 1443 (s), 1067 [s, (S=O)] cm^{-1}. $C_{12}H_{20}OS_3$ (277.49): calcd. C 52.13, H 7.29, S 34.79; found C 52.06, H 7.21, S 34.92.

Reaction of Spirocyclohexyl 1,2,4-Trithiolane 1 with [Pt(η^2-nb)-(PPh_3)$_2$] (4): A portion of spirocyclohexyl-1,2,4-trithiolane **1** (30 mg, 0.11 mmol) was added to a solution of **4** (120 mg, 0.15 mmol) in toluene (10 mL). The solution immediately turned red and was stirred for an additional 3 h at 50 °C. The formation of the dithiolato complex **5** and the thioketone complex **6** in a 1:1 ratio was monitored by TLC. The solvent was reduced to dryness, and the crude product was washed with diethyl ether. The residue was dissolved in thf (10 mL) and filtered through silica gel. The solvent was reduced (to 5 mL), and the mixture was stored in a flask with pentane (10 mL). After 1 d, the dithiolato complex **5** was obtained. Yellow crystals. Yield: 40 mg (64%). M.p. 275 °C dec. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.44 (m, 12 H), 7.30 (m, 6 H), 7.20 (m, 12 H), 1.86 (m, 4 H), 1.44 (m, 4 H), 1.25 (m, 2 H) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 135.0 (t, $J_{C,P}$ = 5.5 Hz), 131.0 (m), 130.5, 127.9 (t, $J_{C,P}$ = 5.2 Hz), 68.1 (s, $^2J_{C,Pt}$ = 58 Hz), 50.5 (s, $^3J_{C,Pt}$ = 23 Hz), 25.9, 23.3 ppm. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ = 24.76 (s, $^1J_{P,Pt}$ = 2971 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3073, 3052, 2925, 2850, 1967 (w), 1903 (w), 1820 (w), 1628 (s br.), 1480, 1434 (s), 1185, 1095 (s), 1028, 1014, 998, 743 (s), 693 (s), 542/525/515/497 (PC_3) cm^{-1}. MS (FAB): *m*/*z* (%) = 865 (0.5) $[M]^+$, 752 (1) $[M - (S{=}C(CH_2)_5)]^+$, 718 $[(Ph_3P)_2Pt]^+$, 307 (100). $C_{42}H_{40}P_2PtS_2$ (865.92): calcd. C 58.26, H 4.66, S 7.41; found C 58.26, H 4.74, S 7.19.

Reaction of Spirocyclohexyl 1,2,4-trithiolane 4-*S*-Oxide 2 with [Pt(η^2-nb)(PPh_3)$_2$] (4): The reaction was carried out in a manner similar to that with the unoxidized spirocyclohexyl 1,2,4-trithiolane **1**, except with spirocyclohexyl-1,2,4-trithiolane 4-*S*-oxide **2** (31 mg, 0.11 mmol). TLC as well as ^{31}P NMR spectroscopy of the crude product showed the formation of a 1:1 mixture of **6** and **7**. In analogy to **5** the sulfenato thiolato complex **7** was isolated by chromatography and subsequent crystallization. Yellow crystals. Yield: 35 mg (52%). M.p. 222 °C dec. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.50–7.18 (m, 30 H), 1.98–1.3 (m, 10 H) ppm. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ = 21.0 (d, $^2J_{P,P}$ = 16, $^1J_{P,Pt}$ = 3324 Hz), 19.8 (d, $^2J_{P,P}$ = 16, $^1J_{P,Pt}$ = 2343 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3054, 2927, 2852, 1969 (w), 1818 (w), 1632 (s br.), 1481, 1435 (s), 1185, 1096 (s), 1019, 998, 995 (br.)/955 (br.) (S=O), 744 (s), 693 (s), 539/523/513/497 (PC_3) cm^{-1}. MS (FAB): *m*/*z* (%) = 882 (4), 767 (24) $[M - (S{=}C(CH_2)_5)]^+$, 718 (20) $[(Ph_3P)_2Pt]^+$. $C_{42}H_{40}OP_2PtS_2$ (881.92): calcd. C 57.20, H 4.57, S 7.27; found C 56.71, H 4.61, S 7.02.

Reaction of Spirocyclohexyl-1,2,4-trithiolane 1-*S*-Oxide 3 with [Pt(η^2-nb)(PPh_3)$_2$] (4): A portion of spirocyclohexyl 1,2,4-trithiolane 1-*S*-oxide **3** (25 mg, 0.09 mmol) was added to a solution of **4** (120 mg, 0.15 mmol) in toluene (10 mL) at room temperature. The colour of the reaction mixture became slightly yellow, and after some minutes, a solid precipitated. The formation of the dithiolato complex **5** and the sulfine complex **8** was confirmed by TLC. The solvent was evaporated, and residue was subjected to column chromatography (THF/hexane, 1:2, SiO_2). The first substantial fraction was assigned to the dithiolato complex **5**, and second fraction contained the sulfine complex **8**; this fraction was collected to yield the pure sulfine complex **8**. White crystals. Yield: 25 mg (40%). M. p. 193 °C dec. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.33 (m, 6 H), 7.24 (m, 12 H), 7.15 (m, 12 H), 2.43 (d, $J_{H,H}$ = 13 Hz), 1.57 (m, 1 H), 1.49 (m, 3 H), 1.41 (m, 2 H), 1.09 (m, 1 H), 1.05 (m, 1 H), 0.84 (m, 1 H) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 134.2 (m, *ipso*-C), 134.0 (m, Ph-C), 129.8 (s, Ph-C), 128.4 (s, Ph-C), 127.8 (m, Ph-C), 83.4 [d, ^2J(C,P) = 53 Hz], 33.0 (s br.), 32.4 (d, $J_{C,P}$ = 6 Hz), 29.1 (d, $J_{C,P}$ = 8 Hz), 28.7, 26.6 ppm. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ = 27.4 (d, $^2J_{P,P}$ = 24, $^1J_{P,Pt}$ = 3817 Hz), 26.4 (d, $^2J_{P,P}$ = 24, $^1J_{P,Pt}$ = 3075 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3072, 3053, 2923, 2847, 1968 (w), 1900 (w), 1816 (w), 1634 (s br.), 1480, 1434 (s), 1183, 1095 (s), 1027, 1011, 997, 983 (S=O), 743 (s), 695 (s), 538/521/510/497 (PC3) cm^{-1}. MS (FAB): *m*/*z* (%) = 850 (15), 719 (100) $[(Ph_3P)_2Pt]^+$. $C_{42}H_{40}OP_2PtS$ (849.86): calcd. C 59.36, H 4.74, S 3.77; found C 59.23, H 4.86, S 3.43.

Synthesis of the Cyclohexanethione Complex 6: Cyclohexanon diethyl ketal (1 g, 5.8 mmol) was dissolved in nonane (30 mL). A stream of hydrogen sulfide was passed through the reaction mixture, and a few drops of concentrated sulfuric acid were added. The mixture became red. After 30 min, the excess hydrogen sulfide was removed by passing a stream of argon through. Solid $NaHCO_3$ was added, and the organic layer was washed with water and dried with Na_2SO_4. The nonane was distilled off under reduced pressure, and cyclohexanthione was trapped in a cooling trap as a solution in nonane. Complex **4** (80 mg, 0.1 mmol) in toluene (10 mL) was added to this solution. The solvent was evaporated, and the residue was washed with diethyl ether, dissolved in thf (15 mL) and filtered over silica gel. The solvent was reduced (to 3 mL), and the mixture was stored in a flask with pentane (20 mL). After some days, pure thioketone complex **6** crystallized. White crystals. Yield: 50 mg (60%). M.p. 234 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.30 (m, 12 H), 7.24–7.11 (m, 18 H); 1.6–1.4 (m, 9 H), 0.87 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.4–133.4 (m), 133.8 (m), 129.2 (m), 127.3 (m), 86.3 (d, $^2J_{C,P}$ = 55 Hz), 43.8, 33.1 (d, $^3J_{C,P}$ = 8.5, $^2J_{C,Pt}$ = 45 Hz), 27.4 ppm. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ = 28.2 (d, $^2J_{P,P}$ = 16, $^1J_{P,Pt}$ = 4600 Hz), 27.0 (d, $^2J_{P,P}$ = 16, $^1J_{P,Pt}$ = 2838 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3052, 2921, 2844, 1964 (w), 1626 (br.), 1479, 1434 (s), 1183, 1094 (s), 1027, 1014, 998, 742, 695 (s), 542/521/511/497 (PC_3) cm^{-1}. MS (FAB): *m*/*z* (%) = 719 (1) $[M - (S{=}C(CH_2)_5)]^+$. $C_{42}H_{40}P_2PtS$ (833.86): calcd. C 60.49, H 4.83, S 3.85; found C 60.19, H 4.82, S 3.67.

Crystal Structure Determination: The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer by

using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects and for absorption effects.[21–23] The structures were solved by direct methods (SHELXS[24]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97[25]). All hydrogen atoms of the structures were included at calculated positions with fixed thermal parameters. With the exception of the carbon atom C1 in compound **8**, all non-disordered, non-hydrogen atoms were refined anisotropically.[25] The oxygen atom in complex **8** had a 50:50 occupancy disorder over two positions, we therefore will not discuss the S–O bond length for the compound. Ortep-3 for Windows[26] was used for the structure representations.

Crystal Data for 5: $C_{42}H_{40}P_2PtS_2$, M_r = 865.89 g mol^{-1}, colourless prism, size 0.02 × 0.02 × 0.02 mm, triclinic, space group $P\bar{1}$, a = 10.4720(2), b = 11.4799(3), c = 16.6495(3) Å, α = 75.337(1), β = 73.691(1), γ = 82.905(1)°, V = 1855.49(7) Å^3, T = –90 °C, Z = 2, $\rho_{calcd.}$ = 1.550 g cm^{-3}, μ(Mo-K_α) = 40.09 cm^{-1}, multiscan, trans$_{min}$: 0.5208, trans$_{max}$: 0.6615, F(000) = 864, 13452 reflections in h(–13/13), k(–14/14), l(–21/20), measured in the range 2.11° ≤ Θ ≤ 27.31°, completeness Θ_{max} = 98.9%, 8262 independent reflections, R_{int} = 0.0189, 7656 reflections with $F_o > 4\sigma(F_o)$, 424 parameters, 0 restraints, R_{1obs} = 0.0233, wR_{2obs} = 0.0560, R_{1all} = 0.0269, wR_{2all} = 0.0579, GOOF = 1.015, largest difference peak and hole: 0.968/–1.061 e Å^{-3}.

Crystal Data for 7: $C_{42}H_{40}OP_2PtS_2$, M_r = 881.89 g mol^{-1}, colourless prism, size 0.02 × 0.02 × 0.01 mm, triclinic, space group $P\bar{1}$, a = 10.5086(2), b = 11.3733(2), c = 16.6699(4) Å, α = 76.040(1), β = 74.247(1), γ = 83.006(1)°, V = 1857.50(7) Å^3, T = –90 °C, Z = 2, $\rho_{calcd.}$ = 1.577 g cm^{-3}, μ (Mo-K_α) = 40.08 cm^{-1}, multiscan, trans$_{min}$: 0.6680, trans$_{max}$: 0.7621, F(000) = 880, 13298 reflections in h(–13/13), k(–14/14), l(–21/20), measured in the range 2.02° ≤ Θ ≤ 27.46°, completeness Θ_{max} = 99.4%, 8451 independent reflections, R_{int} = 0.0184, 8026 reflections with $F_o > 4\sigma(F_o)$, 433 parameters, 0 restraints, R_{1obs} = 0.0223, wR_{2obs} = 0.0545, R_{1all} = 0.0244, wR_{2all} = 0.0556, GOOF = 1.023, largest difference peak and hole: 0.939/–1.383 e Å^{-3}.

Crystal Data for 8: $C_{42}H_{40}OP_2PtS$, M_r = 849.83 g mol^{-1}, colourless prism, size 0.05 × 0.05 × 0.05 mm, orthorhombic, space group *Pbca*, a = 16.0302(3), b = 16.2448(4), c = 27.5941(6) Å, V = 7185.7(3) Å^3, T = –90 °C, Z = 8, $\rho_{calcd.}$ = 1.571 g cm^{-3}, μ (Mo-K_α) = 40.85 cm^{-1}, multiscan, trans$_{min}$: 0.4608, trans$_{max}$: 0.5615, F(000) = 3392, 43387 reflections in h(–20/17), k(–17/21), l(–33/35), measured in the range 2.61° ≤ Θ ≤ 27.54°, completeness Θ_{max} = 99.2%, 8219 independent reflections, R_{int} = 0.1025, 4772 reflections with $F_o > 4\sigma(F_o)$, 429 parameters, 0 restraints, R_{1obs} = 0.0528, wR_{2obs} = 0.0948, R_{1all} = 0.1191, wR_{2all} = 0.1134, GOOF = 0.987, largest difference peak and hole: 2.072/–3.542 e Å^{-3}.

CCDC-655294 (**5**), -655295 (**7**), and -655296 (**8**) 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.

Supporting Information (see footnote on the first page of this article): The IR spectra of complexes **5**–**8** are included.

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[1] a) G. S. Nielsen, L. M. Larsen, L. Poll, *J. Agric. Food Chem.* **2003**, *51*, 1970–1976; b) C.-K. Shu, M. L. Hagerdon, B. D. Mookherjee, C.-T. Ho, *J. Agric. Food Chem.* **1985**, *33*, 438–442; c) R. Gmelin, R. Susilo, G. R. Fenwick, *Phytochemistry* **1981**, *20*, 2521–2523; d) M. Boelens, L. M. Van der Linde, P. J. De Valois, H. M. Van Dort, H. J. Takken, *J. Agric. Food Chem.* **1974**, *22*, 1071–1076; e) H. W. Brinkman, H. Copier, J. J. M. De Leuw, S. B. Tjan, *J. Agric. Food Chem.* **1972**, *20*, 177–181.

[2] a) K. Okuma, *Sulfur Rep.* **2002**, *23*, 209–241; b) G. Mloston, H. Heimgartner in *Targets in Heterocyclic Systems – Chemistry and Properties* (Eds.: O. A. Attanasi; D. Spinelli) , Italian Society of Chemistry, Rome, **2006**, vol. 10, ch. 2.3.

[3] G. Mloston, J. Romanski, H. P. Reisenauer, G. Maier, *Angew. Chem.* **2001**, *113*, 401–404; *Angew. Chem. Int. Ed.* **2001**, *40*, 393–396.

[4] a) R. Huisgen, J. Rapp, *Tetrahedron* **1997**, *53*, 939–960; b) G. Maier, H. P. Reisenauer, J. Romanski, H. Petzold, G. Mloston, *Eur. J. Org. Chem.* **2006**, 3721–3729.

[5] J. Windhager, H. Görls, H. Petzold, G. Mloston, G. Linti, W. Weigand, *Eur. J. Inorg. Chem.* **2007**, 4462–4471.

[6] a) L. C. Song, Z. Y. Yang, Y. J. Hua, H. T. Wang, Y. Liu, Q.-M. Hu, *Organometallics* **2007**, *26*, 2106–2110; b) J. Windhager, M. Rudolph, S. Braeutigam, H. Goerls, W. Weigand, *Eur. J. Inorg. Chem.* **2007**, 2748–2760.

[7] S. J. Wratten, D. J. Falkner, *J. Org. Chem.* **1976**, *41*, 2465–2467.

[8] H. Petzold, S. Bräutigam, H. Görls, W. Weigand, U. Uhlemann, R. Geßner, W. Kiefer, J. Popp, A. Majchrzak, G. Mloston, *Inorg. Chim. Acta* **2004**, *357*, 1897–1908.

[9] a) W. Weigand, R. Wünsch, C. Robl, G. Mloston, H. Nöth, M. Schmidt, *Z. Naturforsch., Teil B* **2000**, *55*, 453–458.

[10] H. Petzold, S. Bräutigam, H. Görls, W. Weigand, M. Celeda, G. Mloston, *Chem. Eur. J.* **2006**, *12*, 8090–8095.

[11] a) T. Shigetomi, H. Soejima, Y. Nibu, K. Shioji, K. Okuma, Y. Yokomori, *Chem. Eur. J.* **2006**, *12*, 7742–7748; b) W. Weigand, S. Bräutigam, G. Mloston, *Coord. Chem. Rev.* **2003**, *245*, 167–175; c) A. Ishii, M. Murata, H. Oshida, K. Matsumoto, J. Nakayama, *Eur. J. Inorg. Chem.* **2003**, 3716–3721; d) W. Weigand, R. Wünsch, *Chem. Ber.* **1996**, *129*, 1409–1419; e) A. Ishii, M. Ohishi, N. Nakata, *Eur. J. Inorg. Chem.* **2007**, 5199–5206.

[12] A. Ishii, M. Saito, M. Murata, J. Nakayama, *Eur. J. Org. Chem.* **2002**, 979–982.

[13] W. Weigand, R. Wünsch, K. Polborn, G. Mlostoń, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1518–1522.

[14] The ^{13}C NMR spectrum of this isolated fraction shows two different sets of 12 signals for each compound. The signals for the quaternary ring carbon atoms appear at 103.5/93.1 and 91.4/86.7 ppm. Attempts to separate the two compounds were in vain.

[15] a) H. Oshida, A. Ishii, J. Nakayama, *J. Org. Chem.* **2004**, *69*, 1695–1703; b) H. Oshida, A. Ishii, J. Nakayama, *Tetrahedron Lett.* **2002**, *43*, 5033–5037.

[16] a) A. Shaver, R. D. Lai, P. H. Bird, W. Wickramasinghe, *Can. J. Chem.* **1985**, *63*, 2555–2558; b) V. W.-W. Yam, P. K.-Y. Yeung, K.-K. Cheung, *J. Chem. Soc. Chem. Commun.* **1995**, 267–269; c) S.-W. A. Fong, T. S. A. Hor, *J. Chem. Soc. Dalton Trans.* **1999**, 639–651.

[17] J. W. Gosselink, G. van Koten, K. Vrieze, B. Zwanenburg, B. H. M. Lammerink, *J. Organomet. Chem.* **1979**, *179*, 411–419.

[18] H. Petzold, H. Görls, W. Weigand, *J. Organomet. Chem.* **2007**, *692*, 2736–2742.

[19] H. Petzold, H. Görls, W. Weigand, J. Romanski, G. Mloston, *Heteroat. Chem.* **2007**, *18*, 584–590.

[20] F. Asinger, M. Thiel, G. Lipfert, *Justus Liebigs, Ann. Chem.* **1959**, *627*, 195–201.

[21] *COLLECT*, Data Collection Software; Nonius B. V., Netherlands, **1998**.

[22] Z. Otwinowski, W. Minor, "Processing of X-ray Diffraction Data Collected in Oscillation Mode" in *Methods in Enzy-*

mology, Vol. 276, Macromolecular Crystallography, Part A (Ed.: C. W. Carter, R. M. Sweet), Academic Press **1997**, pp. 307–326.
[23] *SORTAV*: R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33–38.
[24] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.
[25] G. M. Sheldrick, *SHELXL-97 (Release 97–2)*, University of Göttingen, Germany, **1997**.
[26] *Ortep-3 for Windows*: L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.

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