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Study on Platinum(II) Induced Formation of Dithiiranes

Holm Petzold,[a] Silvio Bräutigam,[a] Helmar Görls,[a] Wolfgang Weigand,*[a] Małgorzata Celeda,[b] and Grzegorz Mloston*[b]

Dedicated to Professor Waldemar Adam on the occasion of his 70th birthday

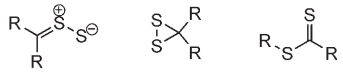
Abstract: The reaction of a series of stable α-chlorinated oligosulfanes **2** and **3** with $[Pt(\eta^2\text{-}C_2H_4)(Ph_3P)_2]$ **1** have been investigated. Starting with the α-chlorodisulfanes **2a**,**b**, the platinum dichloride complex **5** and the side-on bonded thioketone platinum complexes **6a**,**b** were formed. Complex **1** was treated with corresponding trisulfanes **3a**,**b** to give **5**, **6a**,**b** and the dithiolato-complexes **7a**,**b**. We assume that the $\{Pt^0(Ph_3P)_2\}$-complex fragment inserted along the S–S bond to form the unstable intermediate **G**, which decomposed to form the products described above. We could prove that the sterically crowded 1,2,4-trithiolane **8** was not involved in the reaction pathway by treatment of **1** with **8** under the same conditions; after 24 h, **8** was found to be unreacted. X-ray structure analyses were performed on complexes **6a**, **7a** and **7b**.

Keywords: metallacycles · oligosulfanes · platinum · S ligands · thioketone complexes

Introduction

Thiosulfines **A** belong to the class of so-called S-centred 1,3-dipoles, which can be intercepted by C=C-, C≡C- or C=S-dipolarophiles to yield five-membered heterocycles containing two and three sulfur atoms, respectively.[1,2] These reactive intermediates can be generated by sulfur transfer to thioketones[3–5] or by [3+2] cycloreversion of 1,2,4-trithiolanes.[1] In addition, a new method based on the replacement of the oxygen atom in thiocarbonyl S-oxides (sulfines) by sulfur using Lawesson's reagent was recently reported.[6,7]

An equilibrium between thiosulfines **A** and the isomeric dithiiranes **B**, which should convert irreversibly to dithiocarboxylic esters **C** was postulated in 1979[8] and supported by quantum chemical calculations.[9] The existence of the three postulated species **A**, **B** and **C** was confirmed spectroscopically at low temperatures by using 1,2,4-trithiolane as a precursor for the systems **A**/**B**/**C** (R = H).[10]



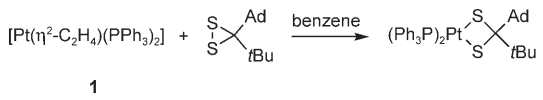
A **B** **C**

Experiments carried out in solution led exclusively to the formation of cyclic S-containing products by interception of thiosulfines **A**.[1] Under these conditions, dithiiranes have neither been detected nor isolated. On the other hand, reactions reported for synthetically available dithiiranes **B**[11] pointed out that they generally did not undergo the postulated rearrangement to intermediates of type **A**. There is only one case known for which the ring opening of a sterically hindered dithiirane led to the [3+2] cycloaddition of the intermediate thiosulfine with a carbonyl group.[11f] However, experiments carried out with $[Pt(\eta^2\text{-}C_2H_4)(Ph_3P)_2]$ complex **1** and dithiiranes at room temperature yielded, by insertion reaction along the S–S bond, the corresponding dithiolato Pt^{II} complex **F**[12] (Scheme 1).

This experiment can be also considered as the best proof for interception of dithiiranes, which may appear as reactive intermediates (Scheme 1).

[a] Dipl.-Chem. H. Petzold, Dr. S. Bräutigam, Dr. H. Görls, Prof. Dr. W. Weigand
Institut für Anorganische und Analytische Chemie
Friedrich-Schiller-Universität Jena
August-Bebel-Strasse 2, 07743 Jena (Germany)
Fax: (+49) 3641-948-102
E-mail: c8wewo@uni-jena.de

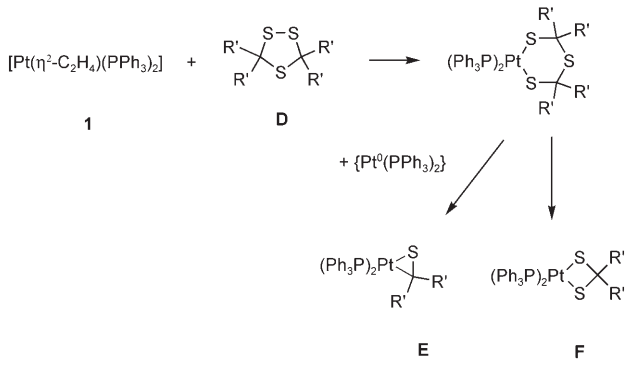
[b] M. Celeda, Prof. Dr. G. Mloston
Section of Heteroorganic Compounds
University of Lodz, Narutowicza 68, 90-136 Lodz (Poland)
Fax: (+48) 42-678-1609
E-mail: gmloston@uni.lodz.pl



Scheme 1. Oxidative addition of a ditiirane to Pt^0 complex **1**. Ad = 1-Adamantyl.

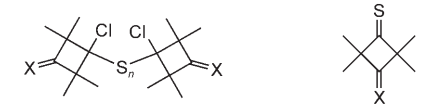
In recent papers, the formation of analogous dithiolato platinum(II) complexes **F** was described. Also the oxidative addition reaction of platinum(0) complexes with naphtho-[1,8-*cd*][1,2]dithioles and dibenzo[1,2]dithiines have to be mentioned in this context.[13] The plausible interpretation of the reaction pathway in the systems containing a S–S bond (for example 1,2,4-trithiolanes **D**) is, however, insertion of $\{Pt^0(Ph_3P)_2\}$ and subsequent intermolecular fragmentation leading to the dithiolato platinum(II) complex **F** and the corresponding thiocarbonyl compound.

The latter compound is intercepted by another equivalent of the complexing agent giving rise to the product of type **E**.[13] In these systems, the equilibrium between **A** and **B** is not necessarily required (Scheme 2).



Scheme 2. Treatment of two equivalents of Pt^0 complex **1** with 1,2,4-trithiolanes **D** to give a 1:1 mixture of thioketone complex **E** and dithiolato complex **F**.

In a continuation of our studies on the complexation reaction of sulfur-rich compounds, we tested a series of α-chlorinated oligosulfanes **2** and **3**, which are promising reaction partners for Pt^0 complexes. These substrates **2** and **3** can be regarded as potential sources of reactive intermediates of type **A** and/or **B**.[14a]



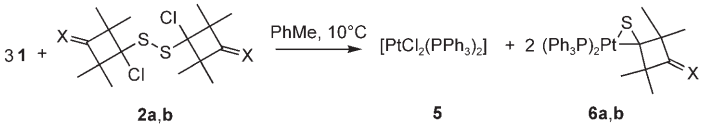
2a: *n*=2 X=O **2b**: *n*=2 X=2Cl
3a: *n*=3 X=O **3b**: *n*=3 X=2Cl

4a: X=O
4b: X=2Cl

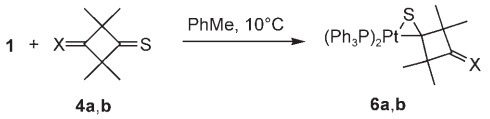
Results and Discussion

The α-chlorinated oligosulfanes **2** and **3** are conveniently available by additions of α-chlorosulfanyl chlorides or α-chlorodisulfanyl chlorides to corresponding thioketones.[14,15]

Reactions of $[Pt(\eta^2\text{-}C_2H_4)(Ph_3P)_2]$ **1** with disulfanes **2a**,**b** were carried out in toluene at 10 °C under an inert argon gas atmosphere. After 1 h, the reactions were complete and the ^{31}P NMR spectra showed the presence of two complexes: one of them was identified as the known compound $[PtCl_2(Ph_3P)_2]$ **5** ($\delta = 18.25$, $^1J(Pt,P) = 3672$ Hz). For the second product, in the case of the experiments with **2a**, the ^{31}P NMR spectrum revealed the presence of the pattern of an AB spin system with two remarkably different coupling constants $^1J(Pt,P) = 2762$ and 4538 Hz, respectively. The ^2J-(P,P) coupling constant was not observed. In the ^1H NMR spectrum, one singlet at $\delta = 0.75$ and one at 1.30 ppm with ^{195}Pt satellites were assigned to the two pairs of chemically nonequivalent methyl groups. The molecular peak $m/e = 875$ suggested that this compound consisted of one molecule of 2,2,4,4-tetramethyl-3-thioxocyclobutanone and one unit of the $\{Pt(Ph_3P)_2\}$ fragment. It was proven by TLC and ^{31}P NMR spectroscopy that this complex is identical to a sample of **6a**, easily prepared by reaction of the corresponding thioketone **4a** with **1** (Schemes 3 and 4). The result of



Scheme 3. Formation the thioketone platinum complexes **6a** and **b**.



Scheme 4. Reactions of thioketones **2a** and **b** with Pt^0 compound **1**.

the X-ray structure analysis confirmed unambiguously the side-on coordination of the thioketone to the $\{Pt(Ph_3P)_2\}$ moiety in **6a** (Figure 1). The C1–S distance of 1.770(4) Å is

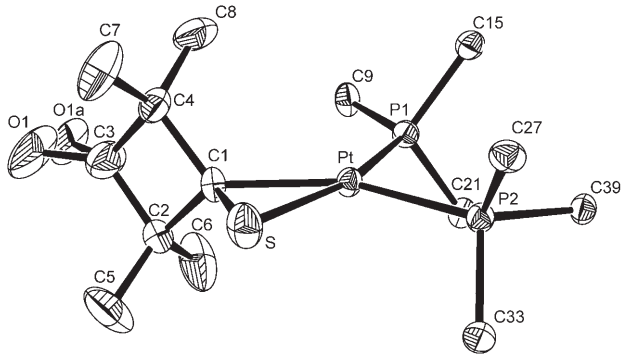
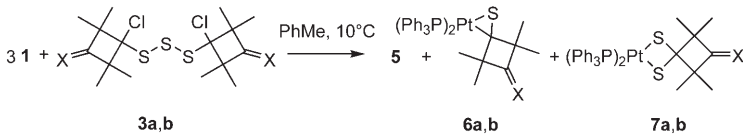


Figure 1. ORTEP[30] drawings of the molecular structure of complex **6a** (hydrogen atoms are omitted for clarity and phenyl groups are represented only by their *ipso*-carbon atoms). Selected bond lengths [Å] and angles [°]: Pt–C1 2.133(4), Pt–S 2.2912(11), S–C1 1.770(4), C1–C2 1.566(6), C2–C3 1.515(6), C3–C4 1.523(7), C4–C1 1.568(6), Pt–P1 2.2719(10), Pt–P2 2.3289(10); C1-Pt-S 47.00(11), S-C1-Pt 71.19(14), C4-C1-C2 91.8(3), P1-Pt-P2 97.64(3).

remarkably longer than that in the uncoordinated thioketone **4a** (1.544(5) Å)[16] and fits well with the data reported for the similar complex with thiobenzophenone [Pt(η^2-SCPh$_2$)(Ph$_3$P)$_2$].[17] This allows the presentation of the product as a platina thiirane derivate **6a**. The nonequivalent Pt–P1 (2.272(1) Å) and the Pt–P2 (2.329(1) Å) bond lengths can be plausibly explained by the different *trans* influences of the sulfur and the carbon atoms, respectively, of the thioketone ligand. The planes of the platina thiirane ring and of the cyclobutanone unit are nearly perpendicular to each other (91.3°; Figure 1). The analogous product **6b** was isolated from the reaction of **1** with the corresponding thioketone **4b** and its structure was elucidated based on spectroscopic data (^{1}H, ^{31}P NMR; MS) supported by results of elemental analysis.

By analogy with the disulfides **2a**,**b**, reactions with trisulfanes **3a**,**b** with **1** were also carried out in toluene at 10 °C and the crude mixtures contained three products in each case. In addition to **5** and **6a**,**b**, new products were obtained as yellow crystals, which could be stored at room temperature without decomposition (Scheme 5).



Scheme 5. Formation of mixtures of thioketone platinum complexes **6a** and **b** and dithiolato platinum complexes **7a** and **b** after the reactions of **1** with trisulfanes **3a** and **b**.

In the ^{1}H NMR spectrum of the new product resulting from the reaction with **3a**, one singlet at 1.19 ppm attributed to four methyl groups was observed. Also the ^{31}P NMR spectrum revealed the presence of one singlet at 24.7 ppm along with the platinum satellites (^1J(Pt,P) = 2985 Hz). These data point out that the molecule is a symmetric one. The FAB-MS contained the $[M+H]^+$ ion at m/z = 908 indicating that in comparison with **6a**, one more sulfur atom is present in the new product. In fact, the elemental analysis confirmed the molecular formula $C_{44}H_{42}OP_2PtS_2$·THF. Due to the typical range of the δ(^{31}P) and the ^1J(Pt,P) values, the structure of the dithiolato platinum(II) complex **7a** can be postulated. The experiments with **3b** afforded, after analogous workup and fractional crystallisation, the expected product **7b**. Structures of dithiolato complexes **7a**,**b** (Figures 2 and 3, respectively) were independently confirmed by means of X-ray diffraction analysis. Key bond lengths are Pt–S1 2.3247(8), Pt–S2 2.3085(8), S1–C1 1.833(3) and S2–C1 1.831(3) Å, which are comparable with those in [Pt(η^2-S$_2$CH$_2$)(R$_3$P)$_2$].[18] A similar complex resulting from the reaction of **1** with a dithiirane 1-oxide is reported to show a significantly longer S–C bond length for the sulfenato unit.[19] In the platina 1,3-dithietane ring, the S1-C1-S2 angle with 101.0(2)° is larger than a symmetrically substituted 1,3-dithietane (94.24(4)°) being a dimer of adamantanethione.[20]

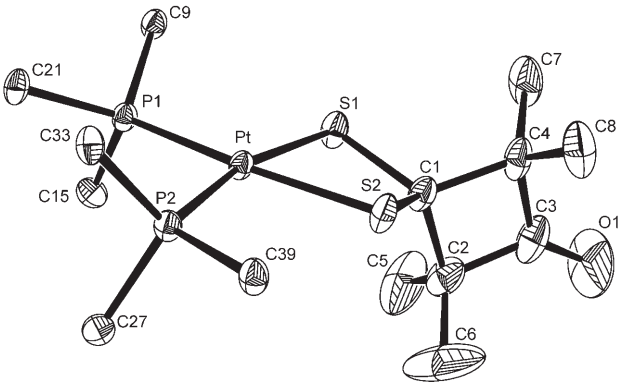
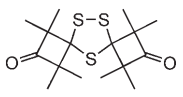


Figure 2. ORTEP[30] drawings of the molecular structure of complex **7a** (hydrogen atoms are omitted for clarity and phenyl groups are represented only by their *ipso*-carbon atoms). Selected bond lengths [Å] and angles [°]: Pt–S2 2.3079(8), Pt–S1 2.3229(9), S2–C1 1.828(3), S1–C1 1.834(3), C1–C2 1.597(4), C2–C3 1.507(5), C3–C4 1.518(5), C1–C4 1.584(4), Pt–P1 2.2903(7), Pt–P2 2.2785(10); S2-Pt-S1 75.24(3), P2-Pt-P1 101.63(3), S1-C1-S2 101.08(13), C2-C1-C4 90.3(2).

In the same moiety, the S1-Pt-S2 angle was determined as 75.22(3)°, which is slightly larger than that in the S-oxidized system (70.4(1)°).[19]

In extension of experiments carried out with the oligosulfanes **2** and **3**, reaction of **1** with the sterically crowded 1,2,4-trithiolane **8** was tested.

A mixture of **8** and **1** was stirred in toluene at room temperature for 24 h. Under these conditions no complexes of the type **6a** or **7a** could be detected in the ^{31}P NMR spectra or by TLC. The reactivity of **8** seemed to be significantly



8

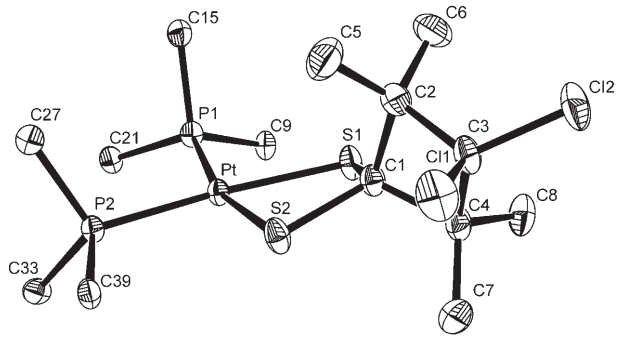


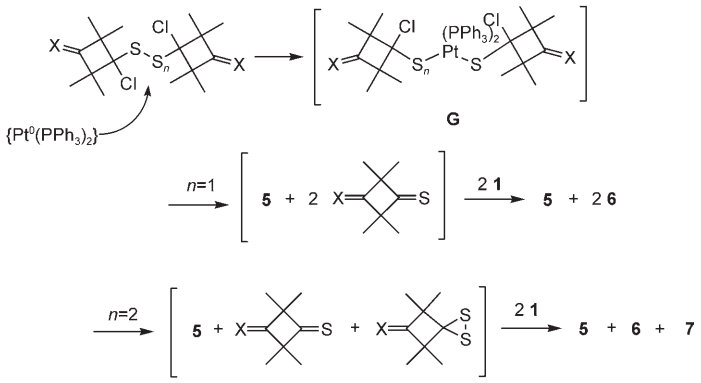
Figure 3. ORTEP[30] drawings of the molecular structure of complex **7b** (hydrogen atoms are omitted for clarity and phenyl groups are represented only by their *ipso*-carbon atoms). Selected bond lengths [Å] and angles [°]: Pt–S2 2.3085(8), Pt–S1 2.3247(8), S2–C1 1.831(3), S1–C1 1.833(3), C1–C2 1.581(4), C2–C3 1.553(5), C3–C4 1.563(5), C1–C4 1.583(4), Pt–P1 2.2915(8), Pt–P2 2.2784(7); S2-Pt-S1 75.22(3), P2-Pt-P1 102.02(3), S1-C1-S2 101.00(15), C2-C1-C4 90.6(2).

reduced in comparison with oligosulfides **2** and **3**. Therefore, it can be also assumed that in the reaction of **1** with **3** no notable amounts of 1,2,4-tritholane **8a**,**b** are formed as intermediates, because otherwise they should be detected in the ^{1}H NMR spectra of the reaction mixture.

Similar products to **6** and **7** are formed by reaction of 1,2,4-trithiolanes of type **D** with $[Pt(\eta^2\text{-}C_2H_4)(Ph_3P)_2]$ **1** at higher temperature. The $\{Pt^0(Ph_3P)_2\}$ fragment reacts by oxidative addition to the S–S bond and subsequently, the expanded platinum-containing ring dissociates to give thioketone complexes of type **E** and dithiolato complexes **F** in a 1:1 ratio.[13,17]

Although the formation of similar products in experiments with **3a**,**b** and 1,2,4-trithiolanes, respectively, were observed, different rationalisations of the reaction pathways were required. It is very likely that in the case of oligosulfanes, the first step occurs by insertion of the platinum atom along the S–S bond to form unstable intermediates of type **G**, this, however, could not be proven experimentally.

Further steps of conversions of these intermediates **G** can not be easily explained, but we propose tentatively, that the intramolecular process releases two equivalents of monothioketone in the case of **2a**,**b** ($n=1$), and in the case of **3a**,**b** ($n=2$), the monothioketone and dithiirane are formed side by side. Each of these compounds is intercepted by **1** to give **6** and **7**, respectively. 1,2,4-trithiolane **8** was not formed in any of the experiments; therefore, the thiosulfine of type **A** is probably not involved in this reaction (Scheme 6).



Scheme 6. Proposed mechanism for the reaction of a $\{Pt^0(PPh_3)_2\}$-complex fragment with di- and trisulfanes **2** and **3**.

Conclusion

In summary, the present study shows that α-chlorinated oligosulfanes **2** and **3** can be used in the presence of $\{Pt^0(Ph_3P)_2\}$ as a source of thioketones and 1,1-dithiolato derivatives. The multistep mechanism of these reactions is initiated by the oxidative addition of the $\{Pt^0(Ph_3P)_2\}$ complex fragment onto the S–S bond. The formation of the 1,1-dithiolato complexes **7a**,**b** results, presumably, by means of an insertion reaction of another $\{Pt^0(Ph_3P)_2\}$-complex fragment into the S–S bond of in situ generated reactive dithiirane derivatives.

Experimental Section

General: Melting points were determined by using an Axiolab microscope with a TMHS 600 heating plate and are uncorrected. ^{1}H, ^{31}P and ^{13}C NMR spectra were determined with Bruker DRX 400 or Bruker DRX 200 spectrometers at 25 °C; chemical shifts are referenced to the protons of the solvent. IR spectra were taken with a Perkin–Elmer System 2000 FTIR spectrometer. Mass spectra were taken with a FINNIGAN MAT SSQ 710 mass spectrometer. Elemental analyses were performed with a LECO CHNS-932. All reactions were performed under argon, and solvents were dried with sodium/benzophenone. Starting materials **1**,[22] **2a**, **2b**, **3a**, **3b**, **8**,[14] **4a**[16] and **4b**[15] were prepared according to the literature procedure.

Treatment of 1,3-bis(1-chloro-2,2,4,4-tetramethyl-3-oxocyclobutan-1-yl)-disulfide (2a) with $[Pt(\eta^2\text{-}C_2H_4)(Ph_3P)_2]$ 1: A solution of $[Pt(\eta^2\text{-}C_2H_4)(Ph_3P)_2]$ **1** (60 mg, 0.08 mmol) in toluene (10 mL) was slowly added to a solution of disulfide **2a** (30 mg, 0.08 mol) in toluene (10 mL) at 10 °C. The yellow suspension was then stirred for 1 h. After this time, the solvent was evaporated to dryness and a mixture of **5** and **6a** contaminated with a small amount of unreacted **2a** was obtained. A similar reaction of **2b** with **1** gave a mixture of **5** and **6b**.

Treatment of 1,3-bis(1-chloro-2,2,4,4-tetramethyl-3-oxocyclobutan-1-yl)-trisulfide (3a) with $[Pt(\eta^2\text{-}C_2H_4)(Ph_3P)_2]$ 1: A solution of $[Pt(\eta^2\text{-}C_2H_4)(Ph_3P)_2]$ **1** (120 mg, 0.16 mmol) in toluene (10 mL) was slowly added to a solution of trisulfide **3a** (33 mg, 0.08 mol) in toluene (10 mL) at 10 °C. The yellow suspension was stirred for 1 h. The solvent was evaporated to dryness. A mixture of **7a**, **6a** and **5** contaminated with a small amount of unreacted **3a** was obtained. To separate **7a**, the residue was dissolved in THF (15 mL), filtrated through Celite to remove **5** and the volume of the solvent was reduced to approximately 5 mL. Pentane (7 mL) was allowed to defuse into the solution over two days. Yellow crystals of **7a** suitable for X-ray analysis were yielded (26 mg, 54 %). M.p. 239–241 °C decomp. (THF/pentane); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=1.19$ (s, 12H; CH_3), 7.05–7.24 (m, 18H), 7.38–7.48 ppm (m, 12H); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta=22.68$ (CH_3), 70.91, 88.03, 125.93 (t, J(C,P) = 10.5 Hz), 130.3, 131.54 (m), 134.78 (t, J(C,P) = 11 Hz), 223.52 ppm (C=O); ^{31}P NMR (81 MHz, $CDCl_3$): $\delta=24.93$ ppm (s, ^1J(P,Pt) = 2962 Hz); IR (CsI): $\tilde{\nu}=$ 1769 (C=O), 542, 525, 514, 496 cm^{-1} (PC_3); MS (FAB): m/z (%): 908 (2) $[M+H]^+$, 837 (8) $[M-O=C=C(Me)_2]^+$, 719 (20; $(Ph_3P)_2Pt^+$), 307 (100); elemental analysis calcd (%) for $C_{44}H_{42}OP_2PtS_2\cdot$THF (980.06): C 58.82, H 5.14, S 6.54; found: C 58.41, H 5.03, S 6.40.

^{31}P NMR spectroscopic investigation of the reaction of 1,3-bis(1-chloro-2,2,4,4-tetramethyl-3-oxocyclobutan-1-yl)trisulfide (3a) with $[Pt(\eta^2\text{-}C_2H_4)(Ph_3P)_2]$ 1: A solution of **1** and **3a** in CD_2Cl_2 (**1**/**3a** 3:1) was prepared at −75 °C and the reaction was observed by recording the ^{31}P NMR spectra in the range of −30 up to +5 °C. Already, at −30 °C the products **5**, **6a**, **7a** and unreacted **1** were detected. The reaction was completed at +5 °C within less than 20 min and the ratio was determined as **5**/**6a**/**7a** 1:1.2:0.8. The sum of the amounts of **6a** and **7a** is twice of the amount of **5**. This fits well to our proposed mechanism. The fact that the amount of **7a** is smaller than that of **6a** is in accordance with the observation reported by A. Ishii et al:[19] Dithiiranes react with **1** yielding the dithiolato complex and the thioketone complex. Thus in our experiment the amount of **6a** must be larger than that of **7a**.

Treatment of 1,3-bis(1-chloro-3,3-dichloro-2,2,4,4-tetramethylcyclobutan-1-yl)trisulfide (3b) with $[Pt(\eta^2\text{-}C_2H_4)(Ph_3P)_2]$ 1: In a similar manner, reaction of trisulfide **3b** (42 mg, 0.08 mol) and $[Pt(\eta^2\text{-}C_2H_4)(Ph_3P)_2]$ **1** (120 mg, 0.16 mol) also yielded a mixture of **7b, 6b** and **5**. Complex **7b** was isolated by using a similar method to that used for **7a**. Yellow crystals; yield: 39 mg, 70 %; M.p. 153 °C decomp. (THF/pentane); ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta=1.34$ (s, 12H, CH_3), 7.18 (m, 12H), 7.29 (m, 6H), 7.43 ppm (m, 12H); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta=25.72$ (CH_3), 61.14, 78.40, 101.68, 127.51 (t, J(C,P) = 10.2 Hz), 130.1, 130.45 (m), 134.47 ppm

(t, J(C,P) = 11 Hz); ^{31}P NMR (81 MHz, $CDCl_3$): δ = 25.25 (s, ^1J(P,Pt) = 2967 Hz); IR (CsI): $\tilde{\nu}$ = 870 (C–Cl), 542, 524, 514, 497 cm^{-1} (PC_3); MS (FAB): m/z (%): 960 (10) $[M-H]^+$, 925 (22) $[M-Cl]^+$, 836 (15) $[M-Cl_2C{=}C(Me)_2]^+$, 719 (40) $\{(Ph_3P)_2Pt\}^+$, 336 (100); elemental analysis calcd (%) for $C_{44}H_{42}Cl_2P_2PtS_2$·THF (1034.97): C 55.70, H 4.87, S 6.20; found: C 55.66, H 4.88, S 6.04.

Syntheses of thioketone complex 6a: A solution of complex **1** (70 mg, 0.1 mmol) in toluene (5 mL) was added slowly to a stirred solution of thioketone **4a** (29 mg, 0.2 mmol) in toluene (5 mL). The clear solution was stirred for 1 h at room temperature. After this time, the solvent was reduced to dryness and the residue was dissolved in THF (3 mL). Pentane was allowed to diffuse slowly into the solution. After two days, white crystals of **6a** were yielded (43 mg, 45%). M.p. 252–255 °C decomp. (THF/pentane); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.75 (s, 6H; CH_3), 1.30 (s, ^4J(H,Pt) = 7.3 Hz, 6H; CH_3), 7.18 (m, 6H), 7.25 (m, 6H), 7.49 (m, 12H), 7.70 ppm (m, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 25.65 (dd, ^4J(C,P) = 3.2 Hz, 7.6 Hz, ^3J(C,Pt) = 39.6 Hz; CH_3), 28.31(d, ^4J(C,P) = 4.5 Hz, ^3J(C,Pt) = 22.1 Hz; CH_3), 69.67, 99.70, 127.98 (dd, J(C,P) = 13.9/12.0 Hz), 128.80 (d, J(C,P) = 12 Hz), 130.01 (d, J(C,P) = 47 Hz), 131.90 (d, J(C,P) = 3.0 Hz), 132.00 (d, J(C,P) = 10 Hz), 133.42 (m), 134.75 (m), 136.13 (m), 223.45 ppm (C=O); ^{31}P NMR (81 MHz, $CDCl_3$): δ = 23.3 (s, ^1J(P,Pt) = 2803 Hz), 26.8 ppm (s, ^1J(P,Pt) = 4587 Hz); IR (KBr): $\tilde{\nu}$ = 1760 (C=O), 549, 520, 511, 496 cm^{-1} (PC_3); MS (DEI): m/z (%): 875 (<1) $[M]^+$, 718 (2) $\{Pt(Ph_3P)_2\}^+$, 262 (100) $[Ph_3P^+]$; elemental analysis calcd (%) for $C_{44}H_{42}OP_2PtS$ (875.89): C 60.34, H 4.83, S 3.66; found: C 59.98, H 4.93, S 3.41.

Syntheses of thioketone complex 6b: Synthesis and isolation procedures were similar to methods described for **6a**. Slightly brown crystals (40 mg, 40%); M.p. >250 °C decomp. (THF/pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (s, 6H, CH_3), 1.28 (s, 6H; CH_3), 7.1 (m, 12H), 7.16–7.25 (m, 12H), 7.52 ppm (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.26 (m, CH_3), 30.68 (m, CH_3), 59.47, 99.8 (d, J(C,P) = 65 Hz), 101.15 (d, J(C,P) = 13.5 Hz), 127.49 (m), 128.26 (m), 129.3 (m), 129.71(m), 133.8 (m), 134.3 (m), 134.8 (m), 136.1 ppm (m); ^{31}P NMR (81 MHz, $CDCl_3$): δ = 23.0 (s, ^1J(P,Pt) = 2747 Hz), 27.3 ppm (s, ^1J(P,Pt) = 4537 Hz); IR (CsI): $\tilde{\nu}$ = 880 (C–Cl), 538, 522, 512, 496 (PC_3) cm^{-1}; MS (FAB): m/z (%): 896 (<1) $[M-Cl]^+$, 720 (16) $\{Pt(Ph_3P)_2\}^+$, 378 (100); elemental analysis calcd (%) for $C_{44}H_{42}Cl_2P_2PtS$·THF (1002.91): C 57.48, H 5.03, S 3.20; found: C 57.35, H 5.00, S 2.95.

Treatment of 1,1,3,3,7,7,9,9-octamethyl-5,10,11-trithiadispiro-[3.1.3.2]undecane-2,8-dione (8) with $[Pt(\eta^2\text{-}C_2H_4)(Ph_3P)_2]$ 1: A solution of $[Pt(\eta^2\text{–}C_2H_4)(Ph_3P)_2]$ **1** (50 mg, 0.06 mmol) in toluene (10 mL) was slowly added to a solution of trithiolane **8** (20 mg, 0.06 mmol) in toluene (10 mL) at 10 °C. The mixture turned red and after 2 h at room temperature an orange solid precipitated, which was insoluble in all common solvents. The suspension was then stirred for an additional 24 h. After this time, the solvent was removed in vacuo to dryness. The ^{1}H NMR spectrum of the resulting mixture showed the typical two signals for **8**. The ^{31}P NMR spectrum showed only signals for $S{=}PPh_3$ and some unidentified signals probably resulting from decomposition of **1**. See also ref. [21].

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refs. [24–26]). The structures were solved by direct methods (SHELXS, ref. [27]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97, ref. [28]). The hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically (ref. [28]). XP (SIEMENS Analytical X-ray Instruments) was used for structure representations. Crystal data for **6a** (ref. [29]): $C_{44}H_{42}OP_2PtS$, $M=875.87\ g\,mol^{-1}$, colourless prism, size: $0.10\times0.09\times0.08\ mm^3$, orthorhombic, space group = *Pbca*, $a=18.1161(3)$, $b=19.0804(3)$, $c=21.8795(4)$ Å, $V=7562.9(2)$ Å^3, $T=-90\,°C$, $Z=8$, $\rho_{calcd}=1.538\ g\,cm^{-3}$, $\mu(Mo_{K\alpha})=38.84\ cm^{-1}$, multiscan, $trans_{min}=0.230$, $trans_{max}=0.295$, $F(000)=3504$, 32307 reflections in $h(-16/23)$, $k(-24/20)$, $l(-27/28)$, measured in the range $1.81\le\Theta\le27.49°$, completeness $\Theta_{max}=99.7\,\%$, 8662 independent reflections, $R_{int}=0.034$, 7314 reflections with $F_o>4\sigma(F_o)$, 452 parameters, 0 restraints, $R1_{obs}=0.032$, $wR^2_{obs}=0.076$, $R1_{all}=0.044$, $wR^2_{all}=0.081$, GOF = 1.045, largest difference peak and hole = 1.936/−1.117 e Å^{-3}. Crystal data for **7a** (ref. [29]): $C_{44}H_{42}OP_2PtS_2{\cdot}C_4H_8O$, $M=980.03\ g\,mol^{-1}$, colourless prism, size $0.02\times0.02\times0.01\ mm^3$, triclinic, space group = *P*(-1), $a=11.589(2)$, $b=13.303(3)$, $c=15.949(3)$ Å, $\alpha=90.38(3)$, $\beta=105.91(3)$, $\gamma=113.48(3)°$, $V=2150.2(7)$ Å^3, $T=-90\,°C$, $Z=2$, $\rho_{calcd}=1.514\ g\,cm^{-3}$, $\mu(Mo_{K\alpha})=34.73\ cm^{-1}$, multiscan, $trans_{min}=0.3426$, $trans_{max}=0.4778$, $F(000)=988$, 16061 reflections in $h(-15/14)$, $k(-17/17)$, $l(-20/20)$, measured in the range $2.62\le\Theta\le27.47°$, completeness $\Theta_{max}=99.2\,\%$, 9761 independent reflections, $R_{int}=0.017$, 9141 reflections with $F_o>4\sigma(F_o)$, 496 parameters, 0 restraints, $R1_{obs}=0.023$, $wR^2_{obs}=0.057$, $R1_{all}=0.026$, $wR^2_{all}=0.058$, GOF = 1.003, largest difference peak and hole = 0.980/−1.051 e Å^{-3}. Crystal data for **7b** (ref. [29]): $C_{44}H_{42}Cl_2P_2PtS_2{\cdot}C_4H_8O$, $M=1034.93\ g\,mol^{-1}$, colourless prism, size = $0.02\times0.02\times0.01\ mm^3$, triclinic, space group = *P*(-1), $a=11.8316(1)$, $b=13.6480(2)$, $c=15.7996(2)$ Å, $\alpha=89.242(1)$, $\beta=71.801(1)$, $\gamma=65.601(1)°$, $V=2187.35(5)$ Å^3, $T=-90\,°C$, $Z=2$, $\rho_{calcd}=1.571\ g\,cm^{-3}$, $\mu(Mo_{K\alpha})=35.34\ cm^{-1}$, multiscan, $trans_{min}=0.3423$, $trans_{max}=0.4731$, $F(000)=1040$, 16617 reflections in $h(-15/15)$, $k(-16/17)$, $l(-20/19)$, measured in the range $2.01\le\Theta\le27.46°$, completeness $\Theta_{max}=97\,\%$, 9717 independent reflections, $R_{int}=0.021$, 8927 reflections with $F_o>4\sigma(F_o)$, 484 parameters, 0 restraints, $R1_{obs}=0.027$, $wR^2_{obs}=0.068$, $R1_{all}=0.032$, $wR^2_{all}=0.070$, GOF = 1.014, largest difference peak and hole: 1.654/−1.420 e Å^{-3}.

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