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Selected cyclic oligosulfides and oligosulfide S-oxides and their reactions with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$

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Contents

Abstract

Syntheses of cyclic organic oligosulfides like dithiiranes, 1,2,4-trithiolanes, 1,2,4,5-tetrathianes, 1,2,3,5,6-pentathiepanes and their mono S-oxides are described. Their reactivity toward the platinum(0) compound $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ has been investigated. Insertion of the platinum(0) moiety into the sulfur–sulfur bond leads to dithiolato, sulfenato-thiolato as well as thiocarbonyl and sulfine platinum complexes. The reaction patterns of the sulfur containing heterocycles with the above metal complex are discussed.

Keywords: Sulfur heterocycles; Platinum(0) complexes; Platinum(II) complexes; Oxidative addition; Dithiirane derivatives

1. Introduction

Natural organic sulfur compounds are widely spread and structurally very diverse [1]. It is known that several organisms produce simple cyclic oligosulfides with different ring sizes: 1,2,4-trithiolane (**1**) has been isolated in extracts of the fungus *Lentinus edodes* Sing. [2] as well as in the red algae *Chondria californica* [3a] and in cultural fluid produced by hyperthermophilic archea (*Thermococcus tadjuricos* and *Thermococcus acidaminovorans*) [4]. The 1,2,4-trithiolane 1-oxide (**2**) and the 1,2,4-trithiolane 4-oxide (**3**), which possess antibiotic activity, can be also detected in extracts of the red algae *C. californica* [3a] (Scheme 1).

1,2,4,5-Tetrathiane (**4**) have been obtained from *L. edodes* as well as from thermococcus cells and have been formed when beef is being boiled [2,4,5]. The green algae *Chara globularia* produces the 5-methylthio-1,2,3-trithiane (**5**) [6] and the highly active antibiotic 1,2,3,5-tetrathiane 5,5-dioxide (**6**) has been isolated in the red algae *C. californica* [3a] (Scheme 2).

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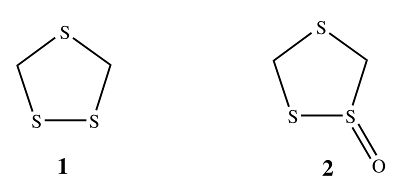
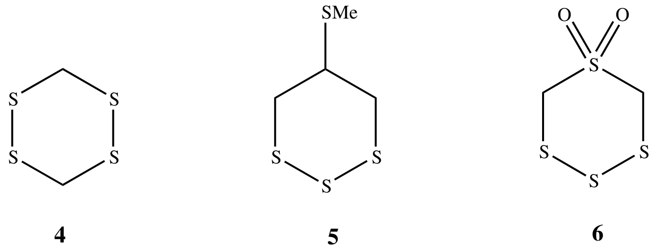
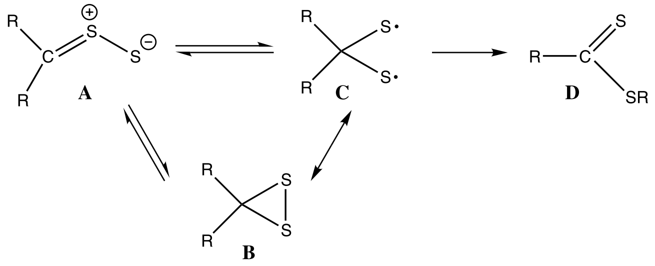


Scheme 1.



Scheme 2.

The seven-membered heterocycles 1,2,4,6-tetrathiepane (**7**), 1,2,3,5,6-pentathiepane (lenthionine) (**8**) and 1,2,3,4,5,6-hexathiepane (**9**) have also been identified in extracts of the fungus *L. edodes* Sing. [2b,2c]. From 5 kg of dried mushrooms, 440 mg of lenthionine, the first cyclic oligosulfide isolated from organisms, were obtained. In addition, the cyclic sulfur compounds **7** and **8** as well as the dioxides **10** and **11** were extracted from *C. californica* [3a]. It was proposed that compounds **7** and **8** were formed by polymerization of the dithiirane **12** as a reactive intermediate originating from lentinic acid **13** by enzymic conversion [7] (Scheme 3).



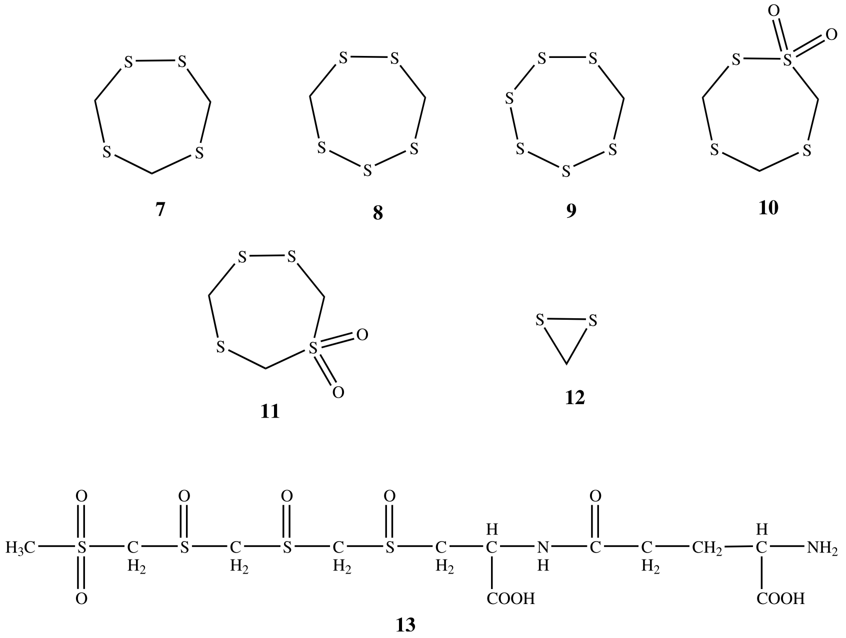
Scheme 4.

From the chemical point of view, some of these oligosulfides are of considerable synthetic and mechanistic interest, particularly as precursors of reactive intermediates like thiosulfines (**A**) and dithiiranes (**B**) [8]. We are interested in investigating the reactivity of platinum(0) complexes with highly sulfurated heterocycles. The interactions of platinum(0) complexes with cyclic oligosulfides lead to remarkable reaction sequences (Scheme 4).

2. Selected methods applied for the synthesis of cyclic oligosulfides

The synthesis and the chemistry of cyclic oligosulfides have been reviewed recently [9]. The present paper touches upon some selected examples.

Thiosulfines (**A**) as reactive intermediates have been under investigation for several years [8]. Twenty years ago, an electrocyclic equilibration of thiosulfines with dithiiranes (**B**) and led to subsequent rearrangement to dithiocarboxylic esters (**D**) [10].



Scheme 3.

2.1. Generation and synthesis of dithiiranes

Recently, the thiosulfine **14** and the dithiirane **12** were generated by flash vacuum pyrolyses (FVP) of the unsubstituted 1,2,4-trithiolane (**1**) and studied by both IR and UV–vis spectroscopy in argon matrices at 10 K. By choice of an appropriate wavelength range during irradiation either a reversible interconversion into isomers **12** and **14**, or the irreversible rearrangement into dithioformic acid (**15**) can be induced [11] (Scheme 5).

Huisgen et al. [8b] established the dissociation equilibrium of the 1,2,4-trithiolane at 60 °C in chloroform in the presence of dimethyl acetylenedicarboxylate. The thiosulfine was intercepted by 1,3-dipolar cycloaddition.

In 1994, J. Nakayama and A. Ishii reported the synthesis of the first isolable dithiirane. Treatment of 6,7-dithiabicyclo[3.1.1]heptane (**16**) with OXONE® ($2KHSO_5{}^{-}KHSO_4{}^{-}K_2SO_4$) or with NaOCl in the presence of $NaClO_4$ yielded the dithiirane **17** [12]. The structure was confirmed by single crystal X-ray structure analysis (Scheme 6).

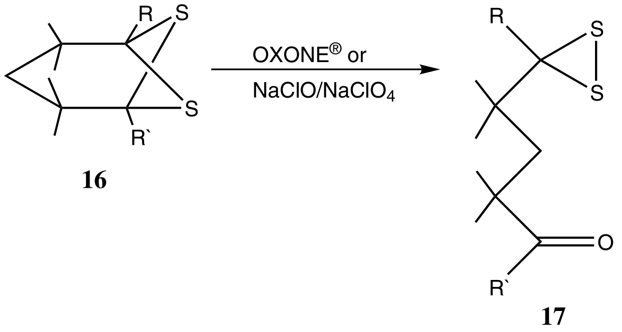
2.2. Synthesis of 1,2,4-trithiolanes

The unsubstituted trithiolane **1** was prepared by reaction of dichloromethane with sodium sulfide $Na_2S \cdot 9H_2O$ and elemental sulfur in the presence of water [2a]. In a similar manner, the tetramethyl derivative **18** was synthesized using di-*iso*butylamine, hydrogen sulfide, elemental sulfur and acetone [13]. The formation of the 3,3,5,5-tetraphenyl-1,2,4-trithiolane (**19**) by slow reaction of two moles of thiobenzophenone with 2,2-diphenylthiirane at room temperature was reported (Scheme 7).

2.3. Synthesis of 1,2,4,5-tetrathianes and 1,2,3,5,6-pentathiepanes

Thiobenzophenone, 2,2,4,4-tetramethyl-3-thiooxocyclobutanone and adamantanethione, respectively, were added to a mixture of flowers of sulfur partially dissolved in acetone in the presence of 1.3 mol% of sodium thiophenoxide based on “S”. The tetrathianes **20**–**22** could be isolated in high yield [14] (Scheme 8).

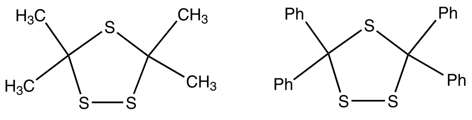
The formation of the pentathiepanes **23** and **24** depend on the thioketone/sulfur ratio. Reaction of the corresponding thioketones with 1.8 g-atom of sulfur and 3 mol% of sodium thiophenoxide in acetone provided the pentathiepanes **23** and **24**, respectively [14] (Scheme 9).



16

17

Scheme 6.



18

19

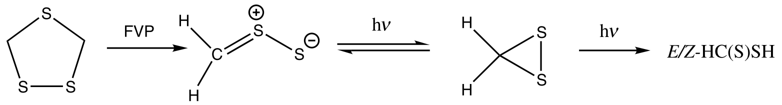
Scheme 7.

3. Monooxidation of cyclic oligosulfides

Ten years ago, the first stable dithiirane 1-oxide was synthesized by oxidation of 6,7-dithiabicyclo[3.1.1]heptane *exo*- and *endo*-6-oxides (**25**) with OXONE® in a mixture of dichloromethane/water to give a mixture of the two diastereoisomers **26** [15] (Scheme 10).

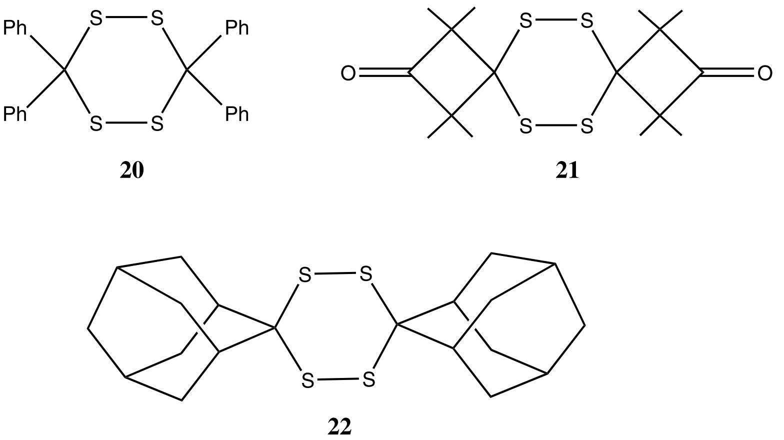
Alternatively, the oxidation of tetrathiolanes (**27**) with dimethyl dioxirane (DMD) yielded aliphatic dithiirane 1-oxides (**28**) [16]. Interestingly, 6-*tert*-butyl-6-phenylpentathiane containing an additional sulfur atom was oxidized with DMD at −20 °C leading to the corresponding 1-oxide (**31**) and 3-oxide (**30**) [17] (Schemes 11 and 12).

Trithiolane (**1**) was oxidized with sodium periodate [3a] or DMD in acetone to give a 1:1 mixture of the regioisomers **2** and **3** [3b]. Both regioisomers could be separated by column chromatography and characterized by ^{1}H-NMR spectroscopic data. In the ^{1}H-NMR spectrum of the 1-oxide (**2**), two coupling patterns of an AB spin system due to the two pairs of diastereotopic protons were observed, whereas one coupling pattern of an AB spin system could be assigned to the 4-oxide (**3**). Under the same conditions, tetramethyl trithiolane (**18**) oxidized by DMD afforded a 3:1 mixture of **32a** and **33**. Finally, the tetraphenyl trithiolane 1-oxide (**32b**) as the single isomer was isolated from **19** when the oxidation was run with mCPBA in dichloromethane at 0 °C. X-ray diffraction confirmed its structure unambiguously [18a]. Recently, it was shown by Ishii et al. [18b], that a

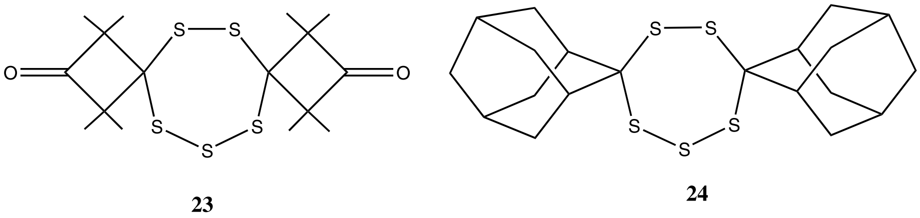


1 **14** **12** **15**

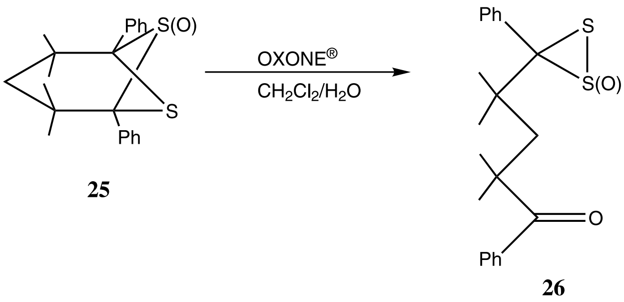
Scheme 5.



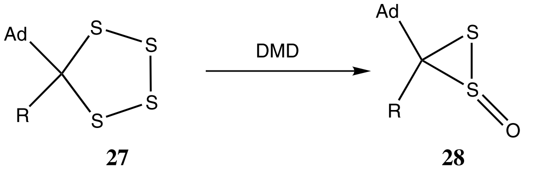
Scheme 8.



Scheme 9.



Scheme 10.



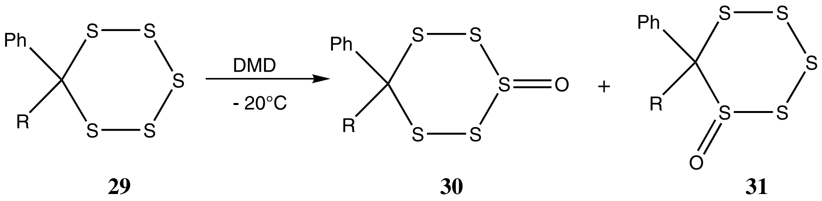
Ad: 1-adamantyl; R = ^{t}Bu, Ad; DMD: dimethyl dioxirane

Scheme 11.

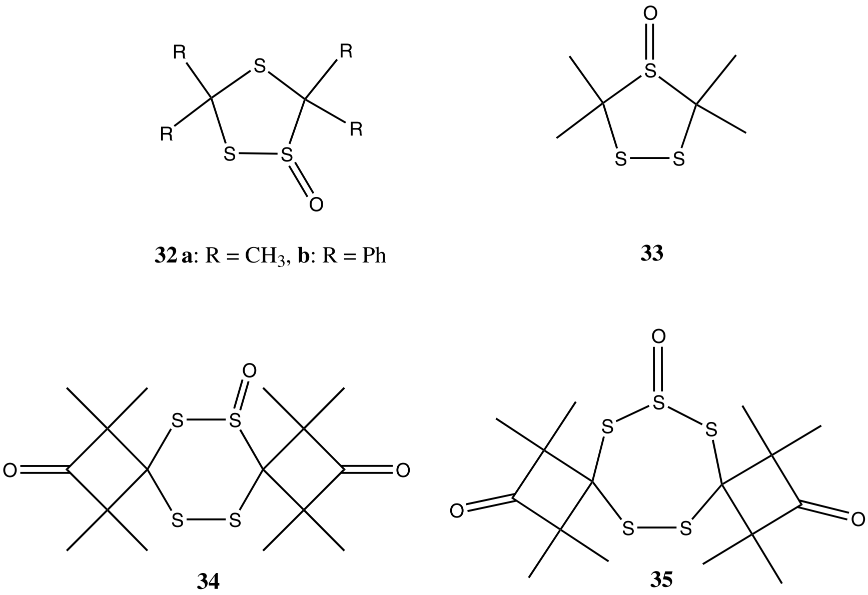
1,2,4-trithiolane with sterically demanding groups can be oxidized with an excess of DMD to give the 1,2-dioxide (*vic*-disulfoxide). Using 1.2 M equivalents of DMD two stereoisomeric 1-monoxides have been isolated. Tetrathiane **20** was oxidized with 1.5 M amounts of trifluoroperacetic acid to give monoxide **34**. When pentathiepane **23** was treated with one equivalent of mCPBA at 0 °C, the ^{1}H-NMR spectrum showed the formation of monoxide **35** as the single product, which could be isolated in 61% yield. In the IR spectra of the above monoxides, characteristic bands in the range of 1100 cm^{-1} are attributed to the ν(S=O) mode [18a] (Scheme 13).

4. Reactions of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ with 1,2,4-trithiolanes, 1,2,4,5-tetrathianes, 1,2,3,5,6-pentathiepine and their S-oxide

In preliminary work [19] (Scheme 14), we have extensively studied the oxidative addition of five- and six-membered thiosulfinic acid S-esters (thiosulfinates) (**36**, **38**) to platinum(0) complexes. It was shown that



Scheme 12.

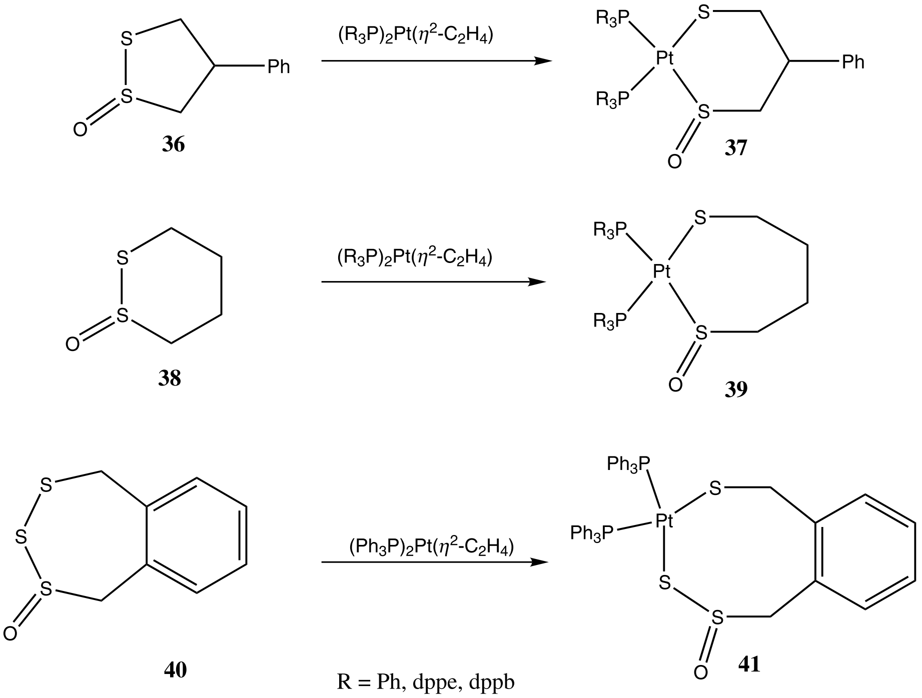


Scheme 13.

insertion of the platinum(0) complex fragment takes place into the S–S(O) linkage yielding complexes with 1-sulfenato-3-thiolato (**37**) [19b] and 1-sulfenato-4-thiolato (**39**) ligands [19a,19d]. When the platinum(0) complex $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ was treated with 2,3,4-benzotrithiepine 1-oxide (**40**) the platinum(0) moiety inserted regiospecifically via oxidative addition into the S–S bond achieving the thiolato thiosulfinato platinum(II) complex **41** [20].

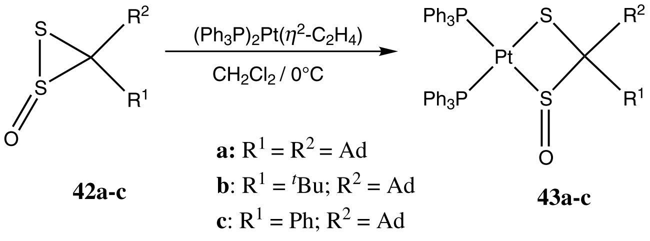
4.1. *Reactions of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ with dithiiranes and dithiirane 1-oxides*

Ishii et al. [21a] have found that treatment of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ with the smallest cyclic thiosulfinates, the dithiirane 1-oxides (**42a–c**) produced 1-sulfenato-1-thiolato platinum(II) complexes (**43a–c**), which were characterized by analytical and spectroscopic data. Also dithiirane **44**



R = Ph, dppe, dppb

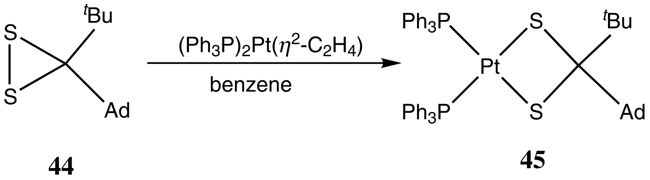
Scheme 14.



42a-c **43a-c**

a: $R^1 = R^2 = Ad$
b: $R^1 = {}^tBu$; $R^2 = Ad$
c: $R^1 = Ph$; $R^2 = Ad$

Scheme 15.



44 **45**

Scheme 16.

reacts with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ via S–S cleavage, giving the dithiolato platinum(II) complex **45** [21b] (Schemes 15 and 16).

4.2. *Reactions of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ with 1,2,4-trithiolanes and their S-oxides*

The 1,2,4-trithiolane (**1**) was treated with two equivalents of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ in toluene and the reaction was followed by ^{31}P-NMR spectroscopy to detect the expected intermediates. It turned out, that an equimolar mixture of two products (**46a**, **47a**) was formed showing coupling patterns of one A_2 and one AB spin system in the ^{31}P-NMR spectrum. In the case of reactions of **18** and **19**, respectively, with two equivalents of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ we were able to isolate the dithiolato platinum(II) complexes (**46b**, **c**) as well as the (η^2-thioketone)platinum compounds (**47b**, **c**), which were characterized additionally by X-ray diffraction (Scheme 17).

For the (η^2-thioketone)platinum compounds (**47b**, **c**) two mesomeric structures can be written. X-ray structure analysis of (**47c**) [22] gave evidence that at least in the solid state the mesomeric formula representing the platinathiirane is the prominent one. The long C–S distance of 1.781(9) Å is quite remarkable considering that the C–S bond length is much shorter in the uncoordinated thioacetone [1.636(9) Å] [23].

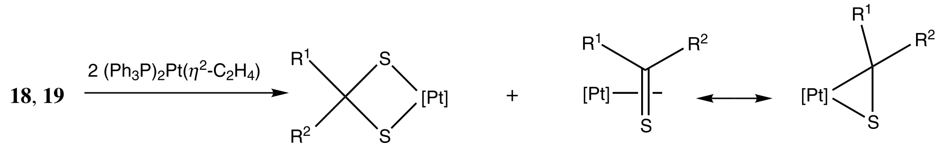
A tentative mechanistic pathway of this type of reaction is depicted in Scheme 18.

As expected, one equivalent of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ was inserted in the first step into the S–S bond of the 1,2,4-trithiolane (**1**). In the ^{31}P-NMR spectrum of a solution of **1** and $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ measured in the range of −50 and −5 °C, a new signal due to complex **48** was observed at 27.3 ppm [$^1J(^{195}Pt^{31}P) = 2824$ Hz]. When the solution was warmed to room temperature the main signal due to **48** became weak and, instead the intensity of two groups of signals increased due to the formation of complexes **46a** [26.4 ppm, $^1J(^{195}Pt^{31}P) = 2891$ Hz] and **47a** [30.0/32.8 ppm, $^1J(^{195}Pt^{31}P) = 3315/4350$, $^2J(^{31}P^{31}P) = 17$ Hz)]. These observations suggested that, **48** was the kinetically controlled product which reacted with another equivalent of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ to give a 1:1 mixture of the dithiolato platinum(II) complex **46a** and the (η^2-thioformaldehyde)platinum complex **47a** in the presence of a catalytic amount of a Lewis-base.

From the preparative and mechanistic point of view reactions of 1,2,4-trithiolane 1-oxide (**32**) and 4-oxide (**33**), respectively, are of considerable interest. Under analogous conditions described for **1**, **18** and **19**, the 1,2,4-trithiolane 1-oxides (**2**) and **32a**, **b** quantitatively reacted with two equivalents of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ yielding the dithiolato platinum(II) **46a–c** and the (η^2-sulfine)platinum complexes **50a–c**. The structures of the latter compounds were determined by comparison of the spectroscopic data with those of a sulfine platinum(II) complex prepared by van Koten et al. [24] and Beck et al. [25] (Scheme 19).

We next examined the treatment of the tetramethyl 1,2,4-trithiolane 4-oxide (**33**) with two equivalents of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ in toluene at 0 °C, which gave a 1:1 mixture of the 1-sulfenato-1-thiolato platinum(II) (**53b**) and the (η^2-thioacetone)platinum complexes (**47b**). As described in Section 4.1, Ishii et al. have found a good route to 1-sulfenato-1-thiolato platinum(II) complexes from oxidative addition of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ to dithiirane 1-oxides [21] (Scheme 20).

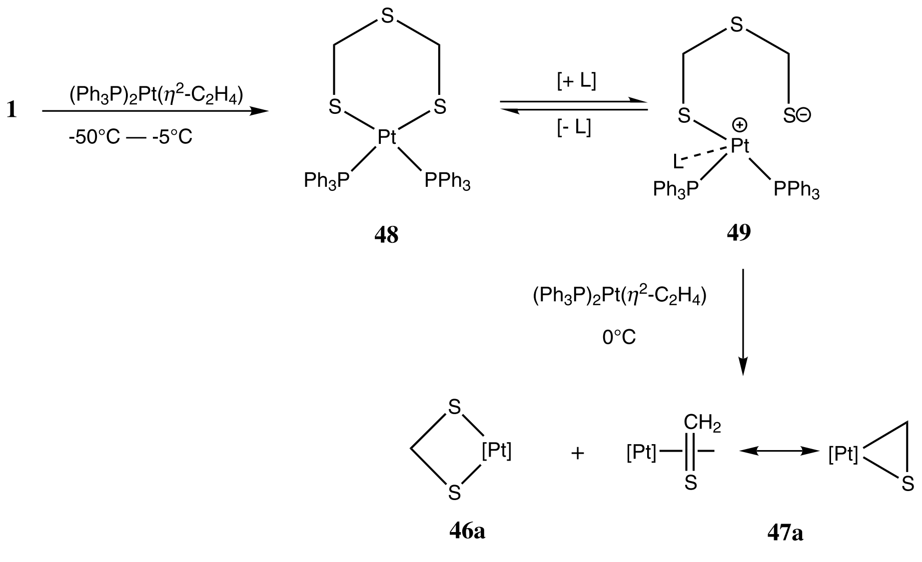
The tentative mechanism in Scheme 20, postulates the intermediate **51a**, **b** formed from the insertion of the platinum(0) moiety into the S–S bond. Unexpectedly, the reaction of 1,2,4-trithiolane 4-oxide (**3**) with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ did not produce the 1-sulfenato-1-thiolato platinum(II) and the (η^2-thioacetone)platinum complexes,



46b,c **47b,c**

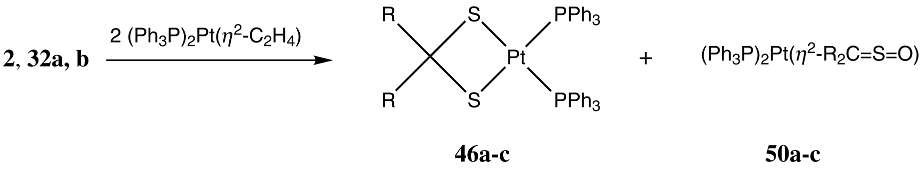
[Pt] = $Pt(PPh_3)_2$ **b**: R = CH_3, **c**: R = Ph

Scheme 17.



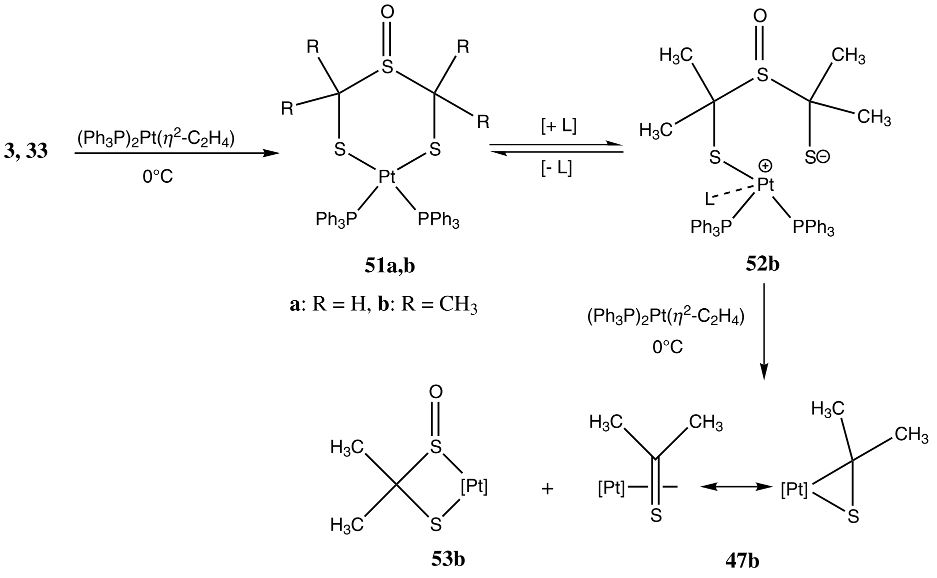
[Pt] = Pt(PPh$_3$)$_2$

Scheme 18.



a: R = H, **b**: R = CH$_3$, **c**: R = Ph

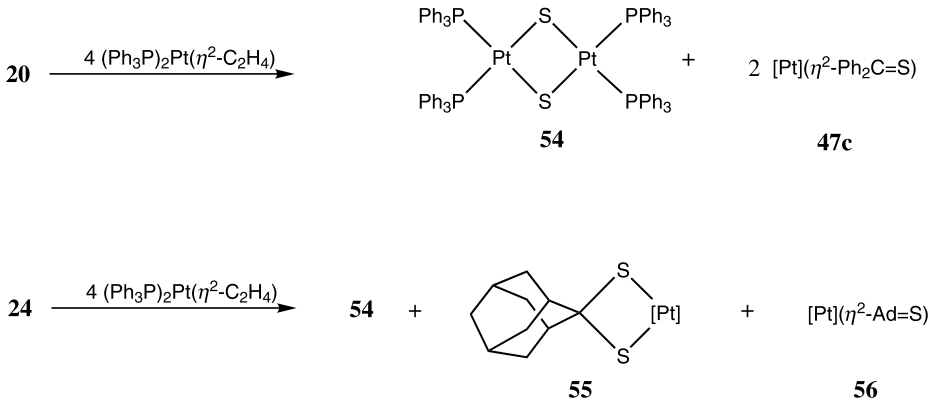
Scheme 19.



a: R = H, **b**: R = CH$_3$

[Pt] = Pt(PPh$_3$)$_2$

Scheme 20.



[Pt]: Pt$(PPh_3)_2$

Ad=S: adamantane thione

Scheme 21.

but the dithiolato platinum(II) complex **51a** could be isolated in high yield. We were able to confirm and to characterize intermediate **51a** by spectroscopic data as well as by X-ray diffraction [26]. Complex **51a** shows high stability and no tendency to react with a further equivalent of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$.

4.3. Reactions of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ with 3,3,6,6-tetraphenyl-1,2,4,5-tetrathiane and bis-adamantane-spiro-1,2,3,5,6-pentathiepane

The reaction of 1,2,4,5-tetrathiane (**20**) with four equivalents of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ induces fragmentation of the cyclic oligosulfide and gives a 2:1 mixture of the (η^2-thiobenzophenone)platinum (**47c**) and the disulfido bridged diplatinum(II) complexes (**54**). Formally, **20** eliminated two moieties of thiobenzophenone and two sulfur atoms, which were intercepted by the platinum(0) complex. Under the some conditions, 1,2,3,5,6-pentathiepane (**24**) combined with four equivalents of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ yields a 1:1:1 mixture of **54**, the dithiolato platinum(II) complex **55** as well as the (η^2-thioketone)platinum compound (**56**). The different compounds could be isolated by fractional crystallization (Scheme 21).

5. Conclusion

This short review gives a compilation of the occurrence, synthesis and reactivity of some cyclic oligosulfides. The principle goal of the experiments is focused on the monoxidation of these sulfur heterocycles and their reactivity toward platinum(0) complexes. In the first reaction step, the platinum(0) complex inserts into the S–S bond followed by a fragmentation of the intermediate in the presence of a further equivalent of platinum(0). The products formed are intercepted by the platinum(0) complex.

Acknowledgements

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