

Synthesis and Reactions of New Dithiopyrroles¹⁾²⁾

by Hans-Dietrich Stachel*^{a)}, Eduard Eckl^{a)}, Elisabeth Immerz-Winkler^{a)}, Christine Kreiner^{a)}, Wolfgang Weigand*^{b)}, Christian Robl^{b)}, Ralf Wünsch^{c)}, Stefan Dick^{c)}, and Norbert Drescher^{c)}

^{a)} Department Pharmazie/Zentrum für Pharmaforschung, Universität München, Butenandtstr. 7, D-81377 München (e-mail: hdsta@cup.uni-muenchen.de)

^{b)} Institut für Anorganische und Analytische Chemie, Friedrich-Schiller-Universität Jena, August-Bebel-Strasse 2, D-07743 Jena (fax: +49 3641 948102; e-mail: wolfgang.weigand@uni-jena.de)

^{c)} Department Chemie, Universität München, Butenandtstr. 9, D-81377 München

Dedicated to Professor *Dieter Seebach* on the occasion of his 65th birthday

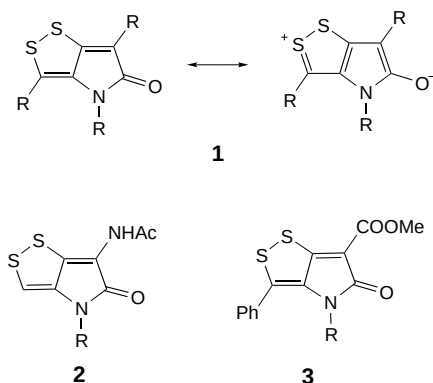
The title compounds were prepared starting from pyrrolinone **4**. Nucleophilic-displacement and ring-closure reactions yielded the dithiopyrrole **5a**, which formed salts with electrophiles (**7, 8**) as well as with bases. The crystal structure of **5a** was determined. Oxidation of the dithioles **5a** and **6a** led to *S*(2)-oxides (**10a, 11a**) and the corresponding *S*(2)-dioxides (**10b, 11b**) depending on reaction conditions. The thiosulfinate **10a** was converted by a ring-opening/ring-closure reaction sequence to the bicyclic sulfinamide **12**. The oxidative addition reactions of [Pt(η^2 -C₂H₄)(PPh₃)₂] (**14**) with the disulfides **5a** and **13** led to the dithiolatoplatinum(II) complexes **15** and **16**, respectively. Complex **16** was characterized structurally. The sulfenato-thiolato complex **17** was synthesized *via* reaction of **14** with the thiosulfinate **10a**. The thiosulfonato Pt^{II} complex **18** was prepared by an oxidative insertion of Pt⁰ into the C–S bond of the corresponding thiosulfonate **10b**. Furthermore, complex **18** was characterized by single-crystal X-ray-diffraction studies.

Introduction. – Bicyclic dithioles of type **1** represent a highly stable kind of cyclic disulfides due to their marked resonance [1]. Several natural substances belong to this type. They were collectively named holothins and pyrrothins, this designation being owed to the long-known antibiotics holomycin (**2**, R = H) and thiolutin (**2**, R = Me) [2]. Groups of holothins with longer side chains are the xenorhabdins [3], the marinols [4], and other substances with potential value in therapy [5]. Recently, we reported the synthesis and chemistry of differently substituted 1,2-dithiopyrrolones of general formula **3** [1][6][7]. Some of these compounds exhibited pharmacologically valuable activities [8]. Supposedly, *S*-oxides of the respective dithiopyrrolones play a decisive role in the physiological activity [1]. It was shown that pyrrothins and other 1,2-dithiopyrroles bearing no substituents in the sulfur ring form highly reactive carbenoid anions, which also may be intermediates in physiological actions [7].

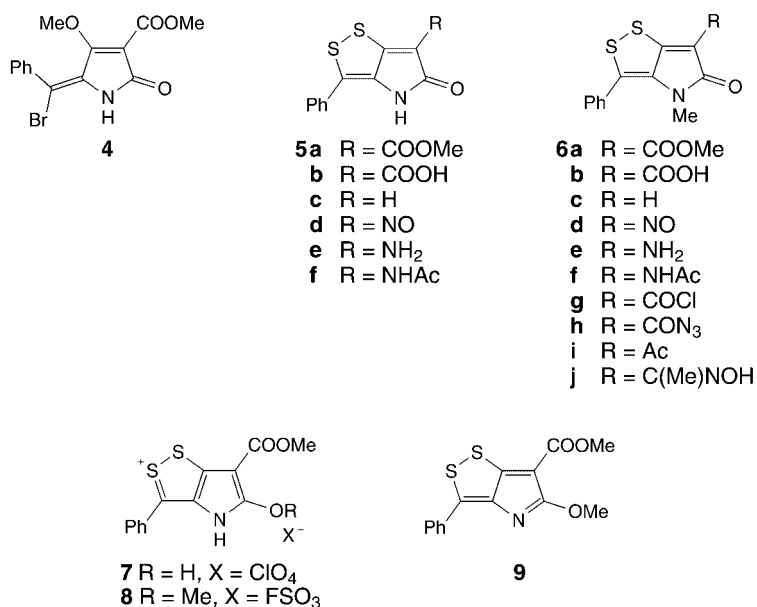
To further investigate the chemical as well as the physiological properties of this type of heterocycle, we have synthesized the phenyl substituted dithiopyrrolones **3**, which we assumed to be more stable against alkali.

¹⁾ Fused 1,2-Dithioles, Part VI.

²⁾ Metal complexes of functionalized sulfur-containing ligands, Part XVIII.



Results and Discussion. – The synthesis started from the known lactam **4** [9]. Upon reaction with Na₂S, nucleophilic displacement first of the MeO group and then of Br occurred to yield a red dithiolate. The salt could not be isolated as an analytically pure substance because of its ready oxidation by O₂ in air. After completing the oxidation with oxidants like I₂ or H₂O₂, the dithiole **5a** was obtained in good yield. The disulfide bond of **5a** was reduced with NaBH₄ to the red dithiolate, which, upon re-oxidation, gave back **5a** quantitatively.



The molecular structure of **5a** (Fig. 1) shows that the molecule is planar, as anticipated; selected bond lengths and angles are given in Table 1. The Ph substituent is out of plane with an angle of 31.5°. The bond lengths of the heterocyclic C-atoms distinctly alternate between double and single bonds. However, the formal double

bonds between C(1)–C(2) and C(3)–C(4) are extended to 136–137 pm and the single bond between C(2)–C(3) is shortened to 143.7(7) pm. The distance between S(1) and S(2) was in the usual range for cyclic disulfides with 208.3(2) pm [10], but the S(2)–C(3) bond (170.9(4) pm) is considerably shorter than the S(1)–C(1) bond (175.6(5) pm). The usual C–S distance was given as 174 pm [11].

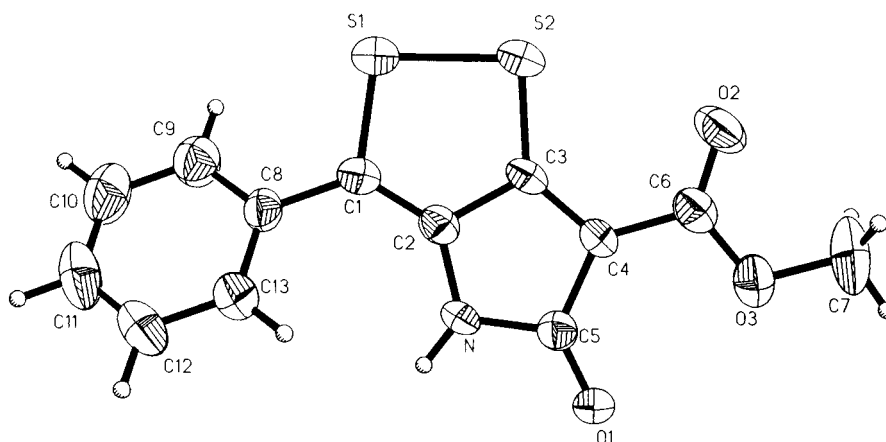


Fig. 1. Molecular structure of **5a** in the crystal

Table 1. Selected Bond Distances [pm] and Bond Angles [°] of **5a**. For atom numbering, see Fig. 1.

Bond distances			
S(1)–S(2)	208.3(2)	C(3)–C(4)	137.2(5)
S(1)–C(1)	175.6(5)	C(2)–N	138.0(5)
S(2)–C(3)	170.9(4)	C(5)–N	139.7(6)
C(1)–C(2)	136.0(5)	C(4)–C(5)	147.0(7)
C(2)–C(3)	143.7(7)		
Bond angles			
C(1)–S(1)–S(2)	96.7(2)	C(2)–C(3)–C(4)	110.2(4)
C(3)–S(2)–S(1)	94.0(2)	C(2)–N–C(5)	110.9(4)
S(2)–C(3)–C(2)	116.4(3)	N–C(5)–C(4)	106.0(3)
C(1)–C(2)–C(3)	119.4(4)	C(3)–C(4)–C(5)	106.6(4)

Due to considerable NH acidity, compound **5a** formed a sparingly soluble potassium salt in MeOH, which reacted with MeI to give the *N*-methylated compound **6a**. The stability of both **5a** and **6a** even toward strong alkali opened the possibility to saponify the ester groups to give the carboxylic acids **5b/6b**. The acids decarboxylated in the presence of copper in quinoline at 150° forming the dithiolopyrrolones **5c/6c**, which are capable of electrophilic substitutions at C(6). Thus, HNO₂ gave the green nitroso derivatives **5d/6d**, which also could be obtained directly from the acids **5b/6b** upon heating with NaNO₂ to 40°. Compounds **5d/6d** were reduced with NaBH₄ to give the amines **5e/6e** in good yields. The acetylated derivatives **5f** and **6f** are new pyrrothins and can be called 3-phenylholomycin or 3-phenylthiolutin, respectively, because of the structural similarity to the natural compounds **2**.

The high stability of the new dithioles allowed a number of textbook reactions to be carried out smoothly. The carboxylic acid **6b** was converted into the acid chloride **6g** and then into the azide **6h**, which upon heating in Ac_2O underwent the *Curtius* rearrangement to give phenylthiolutin **6f**. The dithiopyrrolidone **6c** was acetylated under *Friedel–Crafts* conditions to afford the ketone **6i**. The *Beckmann* rearrangement of oxime **6j** in the presence of PCl_5 took its course under preferential migration of the heterocyclic residue to furnish 3-phenylthiolutin **6f**.

On the other hand, the new dithiopyrrolones showed low basicity. From compound **5a** and HClO_4 in AcOH , the easily crystallized perchlorate **7** was obtained, which hydrolyzed immediately upon contact with H_2O . Analogously, reaction of **5a** and methyl fluorosulfonate gave the salt **8**, the hydrolysis of which with NaHCO_3 led to imino ester **9**. This compound may be regarded as a ‘dithia-azapentalene’ or an ‘aza-pseudoazulene’³⁾ [12] and was also obtained by reaction of **5a** and CH_2N_2 in nearly quantitative yield. The preferential *O*-methylation of carboxylic acid amides with CH_2N_2 is usually interpreted as a hint of the weakened double-bond character of the carbonyl group due to resonance [13].

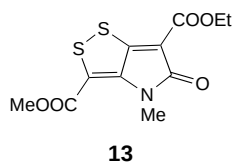
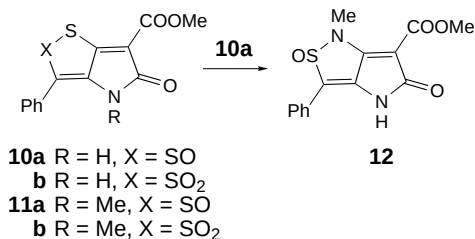
The pyrrothines **5a/6a** were oxidized with 3-chloroperbenzoic acid (*m*CPBA) or with H_2O_2 in AcOH at ambient temperature stepwise to give first the poorly soluble yellow thiosulfinates **10a/11a** and then the orange colored thiosulfonates **10b/11b**. It proved difficult to obtain the thiosulfinates **10a** or **11a** completely free of the corresponding thiosulfonates because, noteworthy, their R_f values hardly differed from each other.

In principle, the oxidation of compounds **5a/6a** could have taken place at *S*(1) or at *S*(2). Both pathways have been observed with other bicyclic dithioles [1]. Proof of the correct structure of the *S*(2)-oxide **10a** was given by a reaction formerly referred to as ‘*S*/*N*-exchange reaction’ of cyclic thiosulfinates [1]. As expected, the reaction of thiosulfinate **10a** with MeNH_2 in the presence of I_2 yielded the isothiazolopyrrolone *S*-oxide **12** (*Scheme*), which is already known and was prepared by an unambiguous synthesis [14]. Likewise, compound **11a** is a *S*(2)-oxide because it was obtained by *N*-methylation of **10a**. From the structures of the monoxides **10a/11a**, it cannot be concluded that the dioxides **10b/11b** also are *S*(2)-oxides. It is known that the oxidation of thiosulfinates to thiosulfonates by electrophilic oxidants may proceed *via* 1,2-disulfoxides and their disproportionation [15]. This pathway of oxidation is hindered by use of a nucleophilic oxidant like NaIO_4 [16]. Since oxidation of the monoxides **10a/11a** with this reagent likewise afforded the dioxides **10b/11b**, their identification as *S*(2)-dioxides gained credence. The structure of **10b** was finally secured by X-ray-diffraction analysis [17].

The thiosulfinates **10a/11a** were deoxygenated either by NaBH_4 or by 1,2-dimethylhydrazine [1] to give the dithioles **5a/6a**. The yellow sulfoxides turn red in day light, most likely due to disproportionation. The propensity of thiosulfinates to disproportionation is well-known from other pyrrothine *S*-oxides [1] as well as from acyclic representatives [18]. MS of the thiosulfinates showed M^+ as well as $[M - \text{O}]^+$ peaks. MS of the dioxides **10b/11b** gave evidence of another route of decomposition by $[M - \text{SO}_2]^+$ fragments beside the molecular-ion peaks. The most prominent peak in the

³⁾ The term ‘pseudoazulene’ was frequently used for cyclopenta[1,2]dithioles.

Scheme

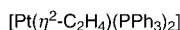
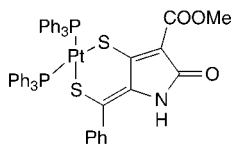
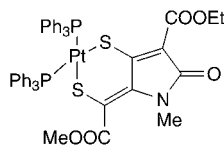
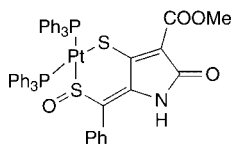
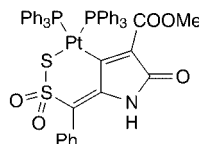


MS fragmentation of all the above dithiols and their *S*-oxides was that of the thiobenzoyl ion (m/z 121).

The chemical behavior of the *S*-oxides **10/11** is characterized by a bicyclic system that is less stable against alkali in comparison with the dithiols **5/6**. As already mentioned, the *S*-oxide **10a** rapidly suffered cleavage of the dithiolo ring with an amine, while the dithiopyrrole **5a** was completely stable under these conditions. The aqueous solutions of the potassium salts of *S*-oxides **10a** or **11a** decomposed quickly at room temperature so that, upon acidification after 30 min, no trace of the starting compound was detectable by thin layer chromatography (TLC). Contrariwise, the dithiopyrrole **5a** could be recovered unchanged from the aqueous solutions of its potassium salt after 3 d. The oxides **10a/b** were converted by CH₂N₂ to the *N*-methylated derivatives **11a/b** exclusively, while the reaction of **5a** with CH₂N₂ afforded the imino ether **9** solely.

The lesser mesomeric stabilization of the oxidized bicyclic systems **10/11** compared to the basis systems **5a/6a** can also be seen in the IR and UV spectra. Comparing the IR spectrum of **5a** with the spectra of the monoxides **10a/11a** and the dioxides **10b/11b**, the C=O absorption bands of all oxides were shifted toward higher wavenumbers, demonstrating lowered resonance participation of the ester groups in the oxides. The longest-wave UV-absorption maxima of the oxides did not show the 'negative solvatochromy' observed in solutions of the dithiols **5a** in solvents of different polarities. Such solvatochromy was said to go along with marked electron delocalization [19].

In preliminary work [20–22], it was shown that cyclic thiosulfonates react readily with Pt⁰ complexes [Pt(η^2 -C₂H₄)(PR₃)₂] *via* insertion of Pt⁰ into the S–S(O) bond, to give chelate complexes containing sulfenato-thiolato compounds. Thus, we studied the oxidative addition of Pt⁰ compounds with the thiosulfonate **10a**. We also extended the study of reactivity of [Pt(η^2 -C₂H₄)(PPh₃)₂] (**14**) toward the disulfides **5a** and **13**, respectively, as well as the thiosulfonate **10b**.

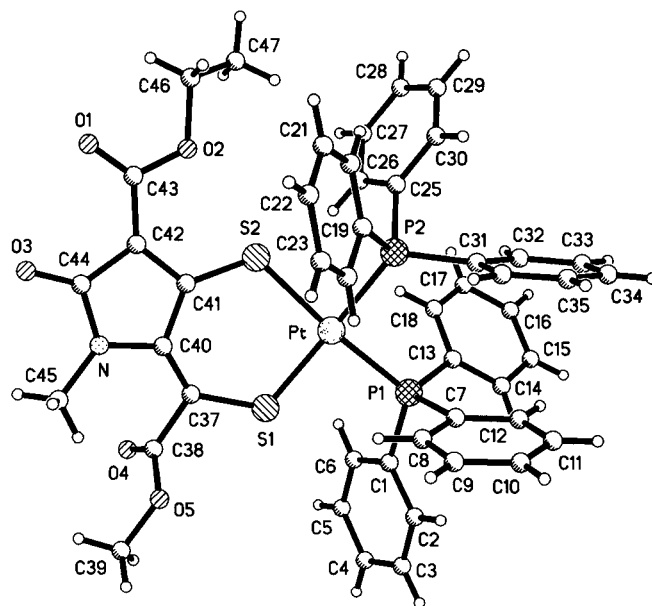
**14****15****16****17****18**

Reaction of a mixture of **14** and **5a** in toluene at room temperature under N_2 afforded the dithiolato complex **15** after workup. The analogous complex **16** was also formed *via* insertion of Pt^0 into the S–S bond of **13**.

Complex **15** and **16** were characterized by NMR spectroscopy and **16** additionally by X-ray structure determination. The ^{31}P -NMR spectrum of **15** and **16**, respectively, showed the characteristic pattern of an *AB* spin system expected for two chemical nonequivalent *cis* phosphines on a square-planar dithiolatoplatinum(II) complex, with resonances at δ 21.08, 22.49 ppm ($^1J(\text{Pt},\text{P}) = 2927, 2939$ Hz, $^2J(\text{P},\text{P}) = 31.5$ Hz; **15**) and δ 22.48, 22.76 ppm ($^1J(\text{Pt},\text{P}) = 2956, 3012$ Hz, $^2J(\text{P}-\text{P}) = 29.8$ Hz; **16**), respectively. In the ^{13}C -NMR spectrum of **15**, the signals assigned to the quaternary C-atoms bound to the S-atoms are at δ 150.8 ppm ($^3J(\text{C},\text{P}) = 5.6$ Hz) and 141.2 ppm ($^3J(\text{C},\text{P}) = 9.2$ Hz).

The molecular structure of the dithiolato complex **16** is shown in Fig. 2; selected bond lengths and angles are given in Table 2. The six-membered cyclic dithiolato platinum(II) complex is distorted from planar, with a dihedral angle of 19.9° between the plane S(1)–Pt–S(2) and the mean plane through S(1)–C(37)–C(40)–C(41)–S(2). The twist angle in the coordination plane between the PtP_2 and the PtS_2 units is 12.5° . Key bond lengths are Pt–S(1) 229.6(2) pm, Pt–S(2) 230.6(2) pm, Pt–P(1) 229.2(2) pm, and Pt–P(2) 231.5(2) pm, which are very similar to those seen with six-membered cyclic dithiolato complexes [23].

By a procedure similar to that used for the disulfides **5a** and **13** [1], the oxidative addition of the thiosulfinate **10a** to **14** yielded the complex **17** after workup. In the ^{31}P -NMR spectrum the typical *AB* pattern for a sulfenato-thiolatoplatinum(II) complex could be observed [22]: it consists of two doublets at δ 19.72 ppm ($^1J(\text{Pt},\text{P}) = 2280$ Hz, $^2J(\text{P},\text{P}) = 30.5$ Hz), for P *trans* to S(O), and δ 22.04 ppm [$^1J(\text{Pt},\text{P}) = 3435$ Hz, $^2J(\text{P},\text{P}) = 30.5$ Hz], for P *trans* to S. This was in accordance with our previous finding that the sulfenato group exhibits a stronger *trans* influence than the thiolato group [24]. In the ^{13}C -NMR spectrum, the signal at 162 ppm is assigned to the C-atom directly bonded to the mono-oxidized S-atom; the resonance signal of this C-atom is shifted downfield by

Fig. 2. Molecular structure of **16** in the crystalTable 2. Selected Bond Distances [pm] and Bond Angles [°] of **16**. For atom numbering, see Fig. 2.

Bond distances			
Pt–S(1)	229.6(2)	S(1)–C(37)	172.6(6)
Pt–S(2)	230.6(2)	S(2)–C(41)	167.0(6)
Pt–P(1)	229.2(2)	C(37)–C(40)	133.3(8)
Pt–P(2)	231.5(2)	C(40)–C(41)	145.1(9)
Bond angles			
S(1)–Pt–S(2)	94.99(6)	P(2)–Pt–S(2)	82.46(6)
P(1)–Pt–P(2)	95.13(6)	P(1)–Pt–S(2)	171.51(7)
P(1)–Pt–S(1)	88.85(6)	P(2)–Pt–S(1)	169.11(6)

11 ppm compared with that of the respective C-atom of the dithiolato complex **15**. The IR spectrum of **17** exhibits a characteristic $\tilde{\nu}(\text{SO})$ band at 999 cm^{-1} , which is in agreement with these absorptions observed for other sulfenato complexes [22]. The $\tilde{\nu}(\text{SO})$ band in complex **17** is shifted 70 cm^{-1} to lower wavenumbers compared to that of the corresponding thiosulfinate **10a**.

In contrast, **14** reacted with the thiosulfonate **10b** via C–S cleavage in toluene at room temperature, giving the thiosulfonato complex **18** as a result of the insertion of Pt(0) into the C–S bond. Interestingly, while organic thiosulfonates $\text{R}'\text{--S--SO}_2\text{--R}$ are known, metal complexes containing the anion $\text{R--SO}_2\text{--S}^-$ as ligands are very rare and limited to few Fe(II) as well as Ru(II) complexes like $[\text{M}(\text{S--SO}_2\text{R})(\text{C})\text{L}_2]$ ($\text{M} = \text{Fe}, \text{Ru}$) [25]. The $\text{R--SO}_2\text{--S}^-$ ligands are isomeric with those in *trans*-[Pt(phthalimido)-

The molecular structure of **18** is shown in *Fig. 3*, selected bond lengths and angles are given in *Table 3*. The Pt coordination plane shows strong distortion from square planarity with a P(1)–Pt–S(2)/S(2)–Pt–C(3) dihedral angle of 22.9°. The distortion, prompted by the steric bulk of the Ph₃P ligands and the bite of the C,*S*-ligand, is reflected in the P(1)–Pt–P(2) and C(3)–Pt–S(2) bond angles of 102.9(1)° and 86.9(2)°, respectively. The Pt–P(1) and Pt–P(2) bond lengths are 235.8(2) and 227.3(2) pm. This confirms that the σ -bonded vinylic C-atom has a higher *trans* influence than the *S*-donor atom. The Pt–C(3) bond length of 204.6(7) pm is similar to that observed in six-membered thiaplatina cycles [27]. The S–S(O)₂ distance in complex **18** is about 9.5 pm smaller than that in the corresponding compound **10b** [17] and comparable to those in other known thiosulfonato complexes [25].

Table 3. Selected Bond Distances [pm] and Bond Angles [°] of **18**. For atom numbering, see Fig. 3.

Bond distances			
Pt–P(1)	235.8(2)	S(1)–O(4)	143.4(4)
Pt–P(2)	227.3(2)	S(1)–O(5)	144.2(5)
Pt–S(2)	236.2(2)	S(1)–C(1)	178.1(7)
Pt–C(3)	204.6(7)	C(1)–C(2)	132.4(8)
S(1)–S(2)	203.4(2)	C(2)–C(3)	153.7(8)
Bond angles			
S(2)–Pt–C(3)	86.9(2)	P(2)–Pt–S(2)	160.6(1)
P(1)–Pt–P(2)	102.9(1)	S(2)–S(1)–O(4)	107.3(2)
P(1)–Pt–S(2)	86.3(1)	S(2)–S(1)–O(5)	112.5(2)
P(2)–Pt–C(3)	88.7(2)	O(4)–S(1)–O(5)	115.5(3)
P(1)–Pt–C(3)	162.4(2)	S(2)–S(1)–C(1)	107.2(2)

Experimental Part

General. M.p.: Gallenkamp melting-point apparatus; uncorrected. IR spectra: Perkin-Elmer PARAGON-1000; KBr pellets; $\tilde{\nu}$ in cm^{-1} . UV/VIS spectra: Kontron Uvikon-810 Anacom-220 or Perkin-Elmer Lambda-20; λ_{max} in nm (log ϵ) in MeOH soln., if not stated otherwise. $^1\text{H-NMR}$ spectra: JEOL GSX-400; δ in ppm rel. to Me_4Si as internal standard, J in Hz, solvent (D_6)DMSO, if not indicated otherwise. MS: Hewlett-Packard 5989A, 70 eV. Flash chromatography (FC): Flash column 250 ml (Baker) with silica gel 0.040–0.063 mm (Merck). Elemental analysis: Heraeus CHNO-Rapid Analyzer or carried out by I. Beetz, Mikroanalytisches Laboratorium, Kronach, Germany.

General Procedure A (GPA). Synthesis of Thiosulfinates from Dithiols. A soln. of 0.27 g (1.1 mmol) of mCPBA (70%) in CH_2Cl_2 (10 ml) was added to a stirred soln. of the dithiol (2 mmol) in CH_2Cl_2 (15 ml), and the mixture was left for 5 h at r.t. The soln. was washed with sat. aq. NaHCO_3 soln. (10 ml) and dried (Na_2SO_4). The solvent was removed *in vacuo*, and the residue (mainly monoxide, traces of dioxide) was crystallized.

General Procedure B (GPB). Synthesis of Thiosulfonates from Dithiols. A soln. of 0.52 g (2.1 mmol) of mCPBA (70%) in CH_2Cl_2 (10 ml) was added to a stirred soln. of the dithiol (1 mmol) in CH_2Cl_2 (15 ml), and the mixture was left at r.t. for the time given. The soln. was washed with sat. aq. NaHCO_3 soln. (10 ml) and dried (Na_2SO_4). The solvent was removed *in vacuo*, and the residue was recrystallized.

General Procedure C (GPC). Reduction of Thiosulfinates with 1,2-Dimethylhydrazine. A soln. of the dithiol *S*-oxide (1 mmol) in CH_2Cl_2 (10 ml) was added to a stirred soln. of 1.8 g (15 mmol) 1,2-dimethylhydrazine dihydrochloride and 6.3 g (30 mmol) 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in anhyd. CH_2Cl_2 (15 ml). After stirring for 2 h at r.t., the soln. was washed repeatedly with 1N H_2SO_4 and, at last, with H_2O and dried (Na_2SO_4). The solvent was removed *in vacuo*, and the residue was recrystallized.

Methyl 4,5-Dihydro-5-oxo-3-phenyl[1,2]dithiolo[4,3-b]pyrrole-6-carboxylate (5a). A soln. of 5.28 g (22 mmol) of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ in MeOH (30 ml) was added to a stirred suspension of 3.38 g (10 mmol) of methyl 5-[bromo(phenyl)methylidene]-2,5-dihydro-4-methoxy-2-oxo-1H-pyrrole-3-carboxylate (**4**) [9] in MeOH (15 ml). The red soln. obtained was heated to reflux for 1 h. After cooling, the resulting red precipitate (of the dithiolate) was isolated, the salt dissolved in the necessary amount of H_2O and stirred for 2 h after addition of 2 ml of aq. soln. (30%) H_2O_2 . The yellow precipitate was isolated and recrystallized. 38% of **5a**. Yellow crystals. M.p. 246–248° (MeOH). UV: 398 (4.213), 265 (3.991), 217 (4.028); pH 10: 413 (4.308), 239 (3.921), 216 (4.020). IR: 3100, 3000, 2970, 1728s, 1685s, 1660s. $^1\text{H-NMR}$: 11.16 (s, 1 H); 7.66 (m, 5 H); 3.81 (s, 3 H). MS: 291 (M^+), 121. Anal. calc. for $\text{C}_{13}\text{H}_9\text{NO}_3\text{S}_2$ (291.35): C 53.59, H 3.11, N 4.81; found: C 53.57, H 3.19, N 4.76.

4,5-Dihydro-5-oxo-3-phenyl[1,2]dithiolo[4,3-b]pyrrole-6-carboxylic Acid (5b). A soln. of 1.45 g (5 mmol) of **5a** in MeOH (20 ml) was heated with 7N KOH (10 ml) at reflux temp. for 3 h. The precipitated salt was collected, and its aq. soln. was acidified with dil. HCl while cooling. The yellow precipitate was isolated and recrystallized. 64% of **5b**. Yellow-green powder. M.p. 268–270° (AcOH). UV: 396 (4.201), 267 (3.860), 217 (3.912). IR: 3400 (br.), 3100, 2940, 1720, 1640. $^1\text{H-NMR}$: 12.38 (s, 1 H); 11.18 (s, 1 H); 7.62 (m, 5 H). MS: 278 ($[M+1]^+$), 122. Anal. calc. for $\text{C}_{12}\text{H}_7\text{NO}_3\text{S}_2$ (277.32): C 51.97, H 2.54, N 5.05, S 23.13; found: C 51.96, H 2.78, N 5.07, S 22.93.

3-Phenyl[1,2]dithiolo[4,3-b]pyrrol-5(4H)-one (5c). A suspension of 1.11 g (4 mmol) of **5b** in quinoline (4 ml) was heated with a small amount of powdered Cu shortly to boiling. After the evolution of CO₂ had ceased, the mixture was cooled, diluted with CH₂Cl₂ (20 ml), filtered, and concentrated *in vacuo*. Upon addition of Et₂O, the product started to crystallize. 55% of **5c**. Orange crystals. M.p. 215–216° (Et₂O). UV: 376 (4.196), 261 (3.915). IR: 3130, 2990, 1670. ¹H-NMR: 10.80 (s, 1 H); 7.70–7.42 (m, 5 H); 5.95 (s, 1 H). MS: 233 (M⁺), 121. Anal. calc. for C₁₁H₇NOS₂ (233.31): C 56.63, H 3.02, N 6.00, S 27.49; found: C 57.63, H 3.39, N 6.56, S 27.89.

6-Nitroso-3-phenyl[1,2]dithiolo[4,3-b]pyrrol-5(4H)-one (5d). An aq. soln. of 0.70 g (10 mmol) of NaNO₂ was added to a suspension of 0.56 g (2 mmol) of **5c** in AcOH (5 ml). Upon heating to 40° for 1 h, the product started to precipitate. 73% of **5d**. Dark green crystals. M.p. 238–240° (AcOH). UV: 485 (3.649), 394 (4.015), 338 (3.861), 279 (4.213). IR: 3330, 2940, 1715, 1660, 1635. ¹H-NMR: 11.52 (s, 1 H); 7.97–7.50 (m, 5 H). MS: 262 (M⁺), 121. Anal. calc. for C₁₁H₆N₂O₂S₂ (262.31): C 50.37, H 2.31, N 10.68, S 24.45; found: C 50.47, H 2.38, N 9.98, S 23.28.

6-Amino-3-phenyl[1,2]dithiolo[4,3-b]pyrrol-5(4H)-one (5e). A soln. of 0.26 g (1 mmol) of **5d** and 0.38 g (10 mmol) of NaBH₄ in MeOH (5 ml) was stirred for 15 min. The precipitate was isolated and recrystallized. 56% of **5e**. Orange crystals. M.p. 205° (MeOH). Dark red precipitate with Ehrlich's reagent. UV: 416 (4.039), 320 (3.817), 275 (4.137). IR: 3380, 3260, 3120, 2960, 1690. ¹H-NMR: 7.58–7.30 (m, 5 H); 4.30 (m, 3 H). MS: 248 (M⁺), 121. Anal. calc. for C₁₁H₈N₂O₂S₂ (248.33): C 53.20, H 3.25, N 11.28, S 25.83; found: C 53.05, H 3.38, N 11.11, S 25.71.

N-(4,5-Dihydro-5-oxo-3-phenyl[1,2]dithiolo[4,3-b]pyrrol-6-yl)acetamide (3-Phenylholomycin, 5f). A soln. of 0.25 g (1 mmol) of **5e** in Ac₂O (3 ml) was left for 30 min at r.t. The precipitate was collected and recrystallized. 68% of **5f**. Red-brown crystals. M.p. 259° (MeOH/CH₂Cl₂ 1:1). UV: 415 (4.141), 322 (3.829), 259 (4.237). IR: 3230, 3160, 3020, 1650, 1635, 1600. ¹H-NMR: 11.00 (s, 1 H); 9.97 (s, 1 H); 7.53 (m, 5 H); 2.07 (s, 3 H). MS: 290 (M⁺), 121. Anal. calc. for C₁₃H₁₀N₂O₂S₂ (290.36): C 53.77, H 3.47, N 9.65, S 22.09; found: C 53.66, H 3.55, N 9.64, S 22.00.

Methyl 4,5-Dihydro-4-methyl-5-oxo-3-phenyl[1,2]dithiolo[4,3-b]pyrrole-6-carboxylate (6a). To a soln. of 0.29 g (1 mmol) of **5a** in anh. DMF (5 ml) were added 0.033 mg (1.1 mmol) of NaH (80%). The mixture was first stirred for 1 h at r.t. and then for another 2 h after addition of MeI (2 ml). The mixture was diluted with CH₂Cl₂ (30 ml) and extracted three times with H₂O. The org. layer was dried (Na₂SO₄) and the solvent removed *in vacuo*. The residue crystallized after addition of a small amount of MeOH. 65% of **6a**. Yellow crystals. M.p. 181–182° (MeOH). UV: 392 (4.218), 218 (4.018). IR: 3040, 2980, 2940, 1725, 1680, 1610. ¹H-NMR: 7.62 (s, 5 H); 3.80 (s, 3 H); 2.88 (s, 3 H). MS: 305 (M⁺), 121. Anal. calc. for C₁₄H₁₁NO₃S₂ (305.37): C 55.06, H 3.63, N 4.59; found: C 55.18, H 3.63, N 4.54.

4,5-Dihydro-4-methyl-5-oxo-3-phenyl[1,2]dithiolo[4,3-b]pyrrole-6-carboxylic Acid (6b). As described for **5b**, with 1.53 g (5 mmol) of **6a** and 4N KOH (10 ml). The saponification was complete after 1 h. 60% of **6b**. Beige powder. M.p. 230–232° (AcOH). UV: 393 (4.118), 219 (3.981). IR: 3450 (br.), 3000 (br.), 1710, 1660, 1630. ¹H-NMR: 12.2 (br. s, 1 H); 7.6 (s, 5 H); 2.90 (s, 3 H). MS: 291 (M⁺), 121. Anal. calc. for C₁₃H₉NO₃S₂ (291.35): C 53.59, H 3.11, N 4.81; found: C 53.72, H 2.98, N 4.93.

4-Methyl-3-phenyl[1,2]dithiolo[4,3-b]pyrrol-5(4H)-one (6c). As described for **5c**, with 0.87 g (3 mmol) of **6b**. The residue was purified by FC (1. petrol ether, 2. Et₂O). The second fraction was collected, and the solvent was removed *in vacuo*. 51% of **6c**. Orange crystals. M.p. 137–138° (Et₂O). UV: 366 (4.271), 244 (sh), 219 (4.018). IR: 3100, 2920, 1655. ¹H-NMR: 7.56 (s, 5 H); 6.03 (s, 1 H); 2.86 (s, 3 H). ¹H-NMR (CDCl₃): 7.48 (s, 5 H); 5.97 (s, 1 H); 3.00 (s, 3 H). ¹³C-NMR (CDCl₃): 173.0 (C(5)); 156.6 (C(6a)); 133.1 (C(3a)); 130.3–128.0 (arom. C); 125.5 (C(3)); 103.7 (C(6)); 28.1 (Me). MS: 247 (M⁺), 121. Anal. calc. for C₁₂H₉NOS₂ (247.34): C 58.27, H 3.67, N 5.66, S 25.93; found: C 58.21, H 3.75, N 5.68, S 25.76.

4-Methyl-6-nitroso-3-phenyl[1,2]dithiolo[4,3-b]pyrrol-5(4H)-one (6d). As described for **5d**, with 0.58 g (2 mmol) of **6c**. 85% of **6d**. Green crystals. M.p. 237–239° (AcOH). UV: 476 (3.693), 394 (4.121), 336 (3.866), 280 (4.013). IR: 3060, 2950, 1700, 1580. ¹H-NMR: 7.93 (s, 5 H); 3.10 (s, 3 H). MS: 275 ([M–1]⁺), 121. Anal. calc. for C₁₂H₈N₂O₂S₂ (276.34): C 52.16, H 2.92, N 10.14, S 23.21; found: C 51.90, H 2.74, N 9.89, S 22.94.

6-Amino-4-methyl-3-phenyl[1,2]dithiolo[4,3-b]pyrrol-5(4H)-one (6e). As described for **5e**, with 0.28 g (1 mmol) of **6d**. 48% of **6e**. Red crystals. M.p. 164–166° (MeOH). UV: 392 (4.193), 309 (3.927), 241 (4.136). IR: 3410, 3310, 2930, 1665, 1585. ¹H-NMR: 7.47 (s, 5 H); 2.83 (s, 3 H). MS: 262 (M⁺), 121. Anal. calc. for C₁₂H₁₀N₂O₂S₂ (262.35): C 54.94, H 3.84, N 10.68, S 24.44; found: C 55.19, H 4.11, N 10.84, S 24.54.

N-(4,5-Dihydro-4-methyl-5-oxo-3-phenyl[1,2]dithiolo[4,3-b]pyrrol-6-yl)acetamide (3-Phenylthiolutin, 6f). Procedure 1. As described for **5f**, with 0.26 g (1 mmol) of **6e**. 95% of **6f**.

Procedure 2. A soln. of 0.30 g (1.5 mmol) of PCl₅ in benzene (10 ml) was added to a stirred soln. of 0.30 mg (1 mmol) of **6j** in benzene (10 ml). After 15 min, the soln. was washed several times with sat. aq. NaHCO₃ soln.

until neutral reaction. The org. phase was dried (Na_2SO_4), the solvent was removed *in vacuo*, and the residue was recrystallized. 63% of **6f**.

Procedure 3. A soln. of 0.33 mg (1 mmol) of **6h** in Ac_2O (5 ml) was heated to 100° for 1.5 h, whereupon the product precipitated. 46% of **6f**.

Data of 6f: Yellow crystals. M.p. $258-261^\circ$ (EtOH). UV: 394 (4.091), 314 (3.919), 252 (4.273). IR: 3260, 3040, 2920, 1670, 1645, 1600. $^1\text{H-NMR}$: 9.98 (s, 1 H); 7.55 (s, 5 H); 2.87 (s, 3 H); 2.07 (s, 3 H). MS: 304 (M^+), 121.

4,5-Dihydro-4-methyl-5-oxo-3-phenyl[1,2]dithiolo[4,3-b]pyrrole-6-carbonyl Chloride (6g). A soln. of 1.45 g (5 mmol) of **6b** in SOCl_2 (6 ml) was heated to reflux (hood) until the gas evolution ceased. The volatile components were removed *in vacuo* at 40° , and the residue was washed several times with Et_2O . 60% of **6g**. Green powder. M.p. $189-191^\circ$. UV: 386 (4.198), 220 (4.023). IR: 2940, 1780, 1765, 1660. MS: 282 ($[M-28]^+$), 121. Anal. calc. for $\text{C}_{13}\text{H}_8\text{ClNO}_2\text{S}_2$ (309.79): C 50.40, H 2.60, N 4.52, S 20.70; found: C 50.21, H 2.55, N 4.38, S 20.50.

6-(Azidocarbonyl)-4-methyl-3-phenyl[1,2]dithiolo[4,3-b]pyrrol-5(4H)-one (6h). A soln. of 0.071 g (1 mmol) of NaN_3 in 1 ml H_2O was added dropwise to a stirred soln. of 0.31 g (1 mmol) of **6g** in acetone (3 ml). The product precipitated and was recrystallized. 72% of **6h**. Yellow crystals. M.p. $133-134^\circ$ (acetone/ H_2O 1:1). UV: 415 (4.298), 248 (4.102). IR: 3050, 2940, 2130, 1705, 1670, 1645, 1600. $^1\text{H-NMR}$: 7.67 (s, 5 H); 2.93 (s, 3 H). MS: 288 ($[M-28]^+$), 121. Anal. calc. for $\text{C}_{13}\text{H}_8\text{N}_4\text{O}_2\text{S}_2$ (316.36): C 49.36, H 2.55, N 17.71, S 20.27; found: C 49.42, H 2.62, N 17.66, S 20.13.

6-Acetyl-4-methyl-3-phenyl[1,2]dithiolo[4,3-b]pyrrol-5(4H)-one (6i). To a suspension of 0.14 g (1 mmol) of powdered anhyd. AlCl_3 in anhyd. 1,2-dichloroethane (5 ml) was added with stirring 0.08 g (1 mmol) of AcCl and 0.24 g (0.95 mmol) of **6c**. After further stirring with exclusion of moisture for 2 h at r.t., the soln. was poured into ice water containing conc. HCl (5 ml), and the mixture was extracted three times with CH_2Cl_2 . The combined org. layers were washed with sat. NaHCO_3 soln. and H_2O and dried (Na_2SO_4). The solvent was removed *in vacuo*, and the residue was recrystallized. 40% of **6i**. Orange crystals. M.p. $178-180^\circ$ (MeOH). UV: 413 (4.115), 263 (3.761), 225 (4.288). IR: 3050, 2940, 1665, 1600. $^1\text{H-NMR}$ (CDCl_3): 7.50 (s, 5 H); 3.05 (s, 3 H); 2.60 (s, 3 H). MS: 289 (M^+), 121. Anal. calc. for $\text{C}_{14}\text{H}_{11}\text{NO}_2\text{S}_2$ (289.38): C 58.11, H 3.83, N 4.84, S 22.16; found: C 58.15, H 3.88, N 4.93, S 22.02.

6-[(1-Hydroxyimino)ethyl]-4-methyl-3-phenyl[1,2]dithiolo[4,3-b]pyrrol-5(4H)-one (6j). A soln. of 0.082 g (1 mmol) of AcONa and 0.070 mg (1 mmol) of hydroxylammonium chloride in 2 ml H_2O was added to a stirred suspension of 0.15 g (0.5 mmol) of **6i** in a mixture of DMSO and MeOH (2 ml each). The mixture was kept over-night at 85° . The product precipitated while cooling. 74% of **6j**. Orange crystals. M.p. $230-232^\circ$ (MeOH). UV: 412 (3.960), 344 (3.877), 258 (4.278). IR: 3260, 1645, 1600. $^1\text{H-NMR}$ (CDCl_3): 7.59 (s, 5 H); 3.07 (s, 3 H); 2.47 (s, 3 H). MS: 304 (M^+), 121. Anal. calc. for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2\text{S}_4$ (304.39): C 55.24, H 3.97, N 9.20, S 21.07; found: C 54.74, H 3.97, N 9.02, S 21.01.

5-Hydroxy-6-(methoxycarbonyl)-3-phenyl-4H-[1,2]dithiolo[4,3-b]pyrrol-2-ium Perchlorate (7). Upon addition of 0.16 g (1.1 mmol) of HClO_4 (70%) to a soln. of 0.29 g (1 mmol) of **5a** in AcOH (5 ml), **7** precipitated at once. The salt was washed once with AcOH and dried for 1 h *in vacuo*. 76% of **7**. Yellowish crystals (AcOH). M.p. $218-220^\circ$ (dec.). UV (HClO_4): 368 (3.970), 285 (3.807), 243 (4.001). IR: 3340 (br.), 3240, 3040, 2920, 2830, 1710, 1660, 1590. $^1\text{H-NMR}$: 11.08 (s, 1 H); 7.55 (s, 5 H); 3.81 (s, 3 H).

5-Methoxy-6-(methoxycarbonyl)-3-phenyl-4H-[1,2]dithiolo[4,3-b]pyrrol-2-ium Fluorosulfonate (8). The soln. of 0.29 g (1 mmol) of **5a** and 1 ml (10 mmol) of methyl fluorosulfonate in anhyd. 1,2-dimethoxyethane (5 ml) was heated at reflux for 15 min. While cooling, **8** precipitated quantitatively and was used immediately for the synthesis of **9**.

Methyl 5-Methoxy-3-phenyl[1,2]dithiolo[4,3-b]pyrrole-6-carboxylate (9). **Procedure 1.** Compound **8** (1 mmol) was stirred with sat. aq. NaHCO_3 soln. (10 ml) and then extracted three times with CH_2Cl_2 . The combined org. layers were dried (Na_2SO_4), and the solvent was removed *in vacuo*. 79% of **9**.

Procedure 2. An ethereal soln. of excessive CH_2N_2 was added to a stirred suspension of 0.30 g (1 mmol) of **5a** in Et_2O (10 ml). A clear soln. was obtained after stirring for 2 h. Removal of the volatile components gave **9** in nearly quantitative yield.

Data of 9: Yellow needles. M.p. $138-139^\circ$ (MeOH). UV: 381 (4.311), 293 (sh), 247 (3.872), 215 (4.165). IR: 3040, 2990, 1717, 1670. $^1\text{H-NMR}$ (CDCl_3): 8.22 (m_c , 2 H); 7.45 (m_c , 3 H); 4.16 (s, 3 H); 3.86 (s, 3 H). MS: 305 (M^+), 121. Anal. calc. for $\text{C}_{14}\text{H}_{11}\text{NO}_3\text{S}_2$ (305.37): C 55.06, H 3.63, N 4.59, S 21.00; found: C 55.32, H 3.59, N 4.49, S 21.03.

Methyl 4,5-Dihydro-2,5-dioxo-3-phenyl-2H-2 λ^4 -[1,2]dithiolo[4,3-b]pyrrole-6-carboxylate (10a). According to *GPA*, with 0.58 g (2 mmol) of **5a**. 46% of **10a**. Faintly yellow crystals. M.p. $226-228^\circ$ (AcOH). UV: 329

(4.210), 226 (4.120). IR: 3280, 3150, 3056, 2957, 1758, 1714, 1655, 1071. $^1\text{H-NMR}$: 11.30 (s, 1 H); 7.57 (m, 5 H); 3.83 (s, 3 H). MS: 307 (M^+), 291 ($[M - 16]^+$), 121. Anal. calc. for $\text{C}_{13}\text{H}_9\text{NO}_4\text{S}_2$ (307.35): C 50.80, H 2.95, N 4.56, S 20.87; found: C 50.71, H 3.01, N 4.62, S 20.57.

Methyl 4,5-Dihydro-2,2,5-trioxo-3-phenyl-2H-2 λ^6 -[1,2]dithiolo[4,3-b]pyrrole-6-carboxylate (10b). A soln. of 1.45 g (5 mmol) of **5a** and 3.92 g (20 mmol) of *m*CPBA (70%) in anhyd. 1,2-dimethoxyethane (30 ml) was heated to reflux for 5 h. The soln. was worked up according to *GP B*. 42% of **10b**. Orange crystals. M.p. 241–243° (AcOH or MeOH). UV: 321 (4.122), 220 (3.902). IR: 3150, 3020, 2948, 1756, 1723, 1690, 1652, 1342, 1145. $^1\text{H-NMR}$: 11.66 (s, 1 H); 7.63 (s, 5 H); 3.86 (s, 3 H). MS: 322 ($[M - 1]^+$), 121. Anal. calc. for $\text{C}_{13}\text{H}_9\text{NO}_5\text{S}_2$ (323.35): C 48.29, H 2.81, N 4.33, S 19.83; found: C 48.17, H 2.73, N 4.44, S 20.05.

Methyl 4,5-Dihydro-4-methyl-2,5-dioxo-3-phenyl-2H-2 λ^4 -[1,2]dithiolo[4,3-b]pyrrole-6-carboxylate (11a). *Procedure 1.* According to *GP A*, with 0.31 g (1 mmol) of **6a**. 52% of **11a**.

Procedure 2. As described for **6a**, by *N*-methylation of **10a** (0.31 g, 1 mmol). 40% of **11a**.

Data of 11a: Faintly yellow crystals. M.p. 211° (AcOH). UV: 316 (4.291), 220 (4.081). IR: 2950, 2920, 1740, 1655, 1580, 1070. $^1\text{H-NMR}$: 7.63 (s, 5 H); 3.86 (s, 3 H); 2.75 (s, 3 H). $^{13}\text{C-NMR}$ (CDCl_3): 167.2 (C(5)); 163.1 (COOMe); 161.3 (C(6a)); 139.5 (C(3a)); 131.0–128.6 (arom. C); 126.6 (C(3)); 113.1 (C(6)); 52.7 (MeO); 28.1 (MeN). MS: 321 (M^+), 305 ($[M - 16]^+$), 121. Anal. calc. for $\text{C}_{14}\text{H}_{11}\text{NO}_4\text{S}_2$ (321.37): C 52.32, H 3.45, N 4.36, S 19.96; found: C 52.53, H 3.19, N 4.43, S 19.66.

Methyl 4,5-Dihydroxy-4-methyl-2,2,5-trioxo-3-phenyl-2H-2 λ^6 -[1,2]dithiolo[4,3-b]pyrrole-6-carboxylate (11b). *Procedure 1.* According to *GP B*, with 0.31 g (1 mmol) of **6a**. 63% of **11b**.

Procedure 2. As described for **6a**, by *N*-methylation of **10b** (0.32 g, 1 mmol). 36% of **11b**.

Data of 11b: Faintly yellow crystals. M.p. 232–234° (MeOH). UV: 314 (4.188), 226 (4.003). IR: 3060, 2960, 1755, 1680, 1590, 1325, 1140. $^1\text{H-NMR}$ (CDCl_3): 7.60 (s, 5 H); 3.98 (s, 3 H); 2.90 (s, 3 H). $^{13}\text{C-NMR}$ (CDCl_3): 165.2 (C(5)); 162.5 (COOMe); 153.7 (C(6a)); 136.2 (C(3a)); 132.0–128.9 (arom. C); 123.6 (C(3)); 113.1 (C(6)); 53.2 (MeO); 28.2 (MeN). MS: 337 (M^+). Anal. calc. for $\text{C}_{14}\text{H}_{11}\text{NO}_5\text{S}_2$ (337.40): C 49.84, H 3.29, N 4.15, S 19.01; found: C 49.73, H 3.39, N 4.20, S 18.95.

Methyl 1,2,4,5-Tetrahydro-1-methyl-2,5-dioxo-3-phenyl-2 λ^4 -pyrrolo[3,2-*c*]isothiazole-6-carboxylate (12). To a stirred ice-cooled soln. of 0.31 g (1 mmol) of **10a** in THF (50 ml) were added first 0.26 g (2 mmol) of I_2 and then dropwise an ethanolic soln. of MeNH_2 (8M, 2.0 ml, 16 mmol). The mixture was allowed to warm to r.t., acidified with 2N H_2SO_4 , and extracted three times with CH_2Cl_2 . The combined org. layers were washed successively with sat. aq. H_2SO_3 soln. and with H_2O , and finally dried (Na_2SO_4). The solvent was removed, and the residue was purified by FC (hexane/AcOEt 1:1). Faintly yellow crystals from MeOH. 41% of **12**. M.p. 240–244° (dec.). M.p. and analytical data identical with [14]. $^1\text{H-NMR}$: 10.98 (s, 1 H); 7.66–7.42 (m, 5 H); 3.74 (s, 3 H); 3.64 (s, 3 H). MS: 304 (M^+), 121. Anal. calc. for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4\text{S}$ (304.32): C 55.25, H 3.97, N 9.21, S 10.54; found: C 55.44, H 4.03, N 9.28, S 10.66.

Reaction of 5a with $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{PPh}_3)_2]$ (14) [28]. Compound **5a** (29 mg, 0.1 mmol) was added to a soln. of **14** (75 mg, 0.1 mmol) in toluene (10 ml). The color changed immediately from yellow to dark brown. After stirring for 1 h at r.t., the soln. was concentrated *in vacuo* to 5 ml. Addition of hexane (20 ml) caused precipitation of the crude material, which was collected by centrifugation and washed twice with Et_2O (20 ml). After drying *in vacuo*, the product was identified as Pt^{II} -complex **15** (64%). Orange-brown powder. M.p. 237–239°. IR: 3100w, 1714s, 1685s, 1655 (br.). $^1\text{H-NMR}$ (CD_2Cl_2): 7.00–7.42 (m, 35 arom. H); 6.95 (s, NH); 3.37 (s, Me). $^{13}\text{C-NMR}$ (CD_2Cl_2): 165.78; 164.70; 150.84 ($J = 5.6$); 141.12 ($J = 9.2$); 135.40; 135.37; 135.31; 135.27; 131.11; 129.11; 128.54; 128.49; 128.23; 128.14; 128.03; 110.33; 50.31. $^{31}\text{P-NMR}$ (CH_2Cl_2): 21.08, 21.49 ($^1J(\text{Pt,P}) = 2939$, 2927, $^2J(\text{P,P}) = 31.5$). Anal. calc. for $\text{C}_{49}\text{H}_{39}\text{NO}_3\text{P}_2\text{PtS}_2$ (1011.02): C 58.21, H 3.89, N 1.39, S 6.34; found: C 58.65, H 3.86, N 1.21, S 6.35.

Reaction of 6-Ethyl 3-Methyl 4,5-Dihydro-4-methyl-5-oxo[1,2]dithiolo[4,3-b]pyrrole-3,6-dicarboxylate (13) [1] with 14 [28]. A soln. of **13** (15 mg, 0.05 mmol) in 10 ml of MeCN was added dropwise to a soln. of **14** (38 mg, 0.05 mmol) in 10 ml of toluene. The color changed from yellow to orange-red. The soln. was stirred at r.t. for 2 h. By a procedure similar to that described for **15**, Pt^{II} -complex **16** was isolated and purified (67%). Orange-brown powder. M.p. 237–239°. IR: 3070w, 2964m, 1711s, 1651s. $^1\text{H-NMR}$ (CD_2Cl_2): 7.14–7.48 (m, 30 arom. H); 3.85 (q, $J = 7.1$, CH_2); 3.03 (s, MeN); 0.83 (t, $J = 7.1$, MeCH_3). $^{31}\text{P-NMR}$ (CH_2Cl_2): 19.76, 22.07 ($^1J(\text{Pt,P}) = 3010$, 2951, $^2J(\text{P,P}) = 31.3$). Anal. calc. for $\text{C}_{47}\text{H}_{41}\text{NO}_3\text{P}_2\text{PtS}_2$ (1021.01): C 55.29, H 4.05, N 1.37, S 6.28; found: C 55.85, H 3.96, N 1.29, S 6.35.

Reaction of 10a with 14 [28]. By a procedure similar to that for **15**, with 21 mg (0.1 mmol) of **10a** and 75 mg (0.1 mmol) of **14** in 10 ml of toluene, Pt^{II} -complex **17** was prepared and purified to give a carmine product (68%). M.p. 170–172°. IR: 3441w, 3051w, 1721s, 1709s (sh), 999m. $^1\text{H-NMR}$ (CD_2Cl_2): 7.00–7.55 (m, 35 arom. H); 6.73 (s, NH); 3.53 (s, Me). $^{13}\text{C-NMR}$ (CD_2Cl_2): 168.45; 163.90; 162.02; 140.85; 135.93 ($J = 5.6$); 135.14;

135.03; 134.91; 134.80; 131.61; 131.51; 131.49; 129.78; 129.13; 128.97; 128.90; 128.86; 128.79; 116.26 ($J = 4.2$); 51.31. ^{31}P -NMR (CH_2Cl_2): 19.72, 22.04. ($^1J(\text{Pt},\text{P}) = 2280$, $^2J(\text{P},\text{P}) = 30.5$). Anal. calc. for $\text{C}_{49}\text{H}_{39}\text{NO}_4\text{P}_2\text{PtS}_2$ (1027.02): C 57.31, H 3.83, N 1.36, S 6.33; found: C 56.95, H 4.08, N 1.42, S 6.48.

Reaction of 10b with 14 [28]. Compound **10b** (22 mg, 0.07 mmol) was added to a soln. of **14** (50 mg, 0.07 mmol) in toluene (10 ml). The color changed immediately from yellow to light brown. The soln. was stirred at r.t. for 10 h, while a yellow solid began to precipitate. The precipitate was collected by centrifugation, washed twice with 20 ml of Et_2O , and dried *in vacuo*. The product was identified as Pt^{II} -complex **18** (82%). Ochre-yellow powder. M.p. 272–273; IR: 3443m, 3018m, 1717s, 1706s, 1628m, 1273s, 1094s. ^1H -NMR (CD_2Cl_2): 7.10–7.75 (m , 35 arom. H); 6.05 (s , NH); 3.41 (s , Me). ^{13}C -NMR (CD_2Cl_2): 166.44 ($J = 8.5$); 166.24; 143.63 ($J = 6.9$);

Table 4. Summary of Crystal Data for the Complexes **5a**, **16**, and **18**

	5a	16	18
Formula	$\text{C}_{13}\text{H}_9\text{NO}_3\text{S}_2$	$\text{C}_{47}\text{H}_{41}\text{NO}_5\text{P}_2\text{PtS}_2$	$\text{C}_{49}\text{H}_{39}\text{NO}_5\text{P}_2\text{PtS}_2 \cdot 2.12 \text{ H}_2\text{O}$
Color	red	yellow	yellow
Crystal size [mm]	$0.04 \times 0.10 \times 0.22$	$0.14 \times 0.42 \times 0.46$	$0.50 \times 0.50 \times 0.40$
Crystal system	monoclinic	triclinic	monoclinic
Space group	$I2/a$ (no. 15)	$P\bar{1}$	$P2_1/n$
Unit-cell dimensions			
a [Å]	26.657(13)	12.605(1)	13.224(3)
b [Å]	3.9193(13)	13.272(1)	16.215(3)
c [Å]	27.424(13)	14.741(1)	22.671(4)
α [°]	90	78.96(1)	90
β [°]	116.74(3)	75.53(1)	103.917(14)
γ [°]	90	66.25(1)	90
Volume of unit cell [Å ³]	2559(2)	2157.9(3)	4718.6(15)
Z	8	2	4
Formula weight	291.3	1020.96	1081.2
Density (calc.) (Mg/m ³)	1.512	1.571	1.518
Absorption coefficient (mm ^{−1})	0.400	3.469	3.204
$F(000)$	1200	1020	2150.72
Radiation	MoK_α	MoK_α	MoK_α
Temperature (K)	295	295	295
θ_{max} [°]	25	25	25
Reflections collected	5350	7923	9008
Independent reflections	2264	7550	8282
R_{int}	0.0209	0.0240	0.0213
$ F > 3\sigma_{ F }$	1486		7153
$I > 2\sigma_I$		6461	
Quantity minimized	$\Sigma(F_o - F_c)^2$	$\Sigma(F_o ^2 - F_c ^2)^2$	$\Sigma(F_o - F_c)^2$
Extinction correction	empirical	no	no
Absorption correction	numerical	numerical	numerical
Transmission min./max.	0.955/0.984	0.328/0.568	0.212/0.344
Weighting scheme	$w = \sigma^{-2}$	$w = \sigma^{-2}$	$w = \sigma^{-2}$
Parameters refined	179	525	690
Residuals			
R^a)	0.0601	0.0365	0.0421
wR^b)	0.0387	0.0667	0.0358
s^c)	1.72	1.616	2.64
Largest features of the final difference Fourier synthesis [$\text{e} \cdot \text{\AA}^{-3}$]	+ 0.42/− 0.38	+ 0.89/− 0.87	+ 0.91/− 1.60

^a) $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. ^b) $wR = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$ and the $|F|^2$ equiv., resp. ^c) $s = \Sigma w(|F_o| - |F_c|)^2 / (N - N_p)$ with N = number of reflections, N_p = number of parameters; and the $|F|^2$ equiv.

135.37; 135.25; 135.15; 134.69; 132.88 ($J = 4.9$); 131.58; 131.53; 131.12; 131.00; 130.95; 129.88; 129.13; 129.56; 129.26; 128.97; 128.87; 125.84; 51.90. ^{31}P -NMR (CH_2Cl_2): 7.47, 12.56 ($^1J(\text{Pt}, \text{P}) = 2054$, $^2J(\text{P}, \text{P}) = 20.7$). Anal. calc. for $\text{C}_{40}\text{H}_{30}\text{NO}_5\text{P}_2\text{PtS}_2$ (1043.02): C 56.43, H 3.77, N 1.34, S 6.15; found: C 56.02, H 3.98, N 1.25, S 6.21.

X-Ray-Structure Analysis of 5a, 16, and 18. Intensity data have been collected on a *Siemens P4 (16)* and a *Siemens R3m/V (5a, 18)* four-circle diffractometer, resp., with variable scan speed in ω -scan mode with graphite monochromated MoK_α radiation. Background counts were taken with stationary crystal and stationary counter at beginning and end of scan, each for 1/4 of the total scan time. A face-indexed numerical absorption correction was applied. The phase problem was solved by means of the direct methods of the SHELXTL program suite. Full-matrix least-squares refinement was based on $|F|^2$ (**16**) and $|F|$ (**5a, 18**), resp. The non-H-atoms have been refined with anisotropic displacement parameters. H-atoms have been placed into calculated positions in the final stages of refinement. Some disorder of H_2O of crystallization was encountered in **18**. Further crystallographic data are compiled in Table 4.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as deposition Nos. CCDC-198233 (**16**), 198234 (**5a**), and 198235 (**18**). Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk).

We gratefully acknowledge financial support of the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie*.

REFERENCES

- [1] J. E. Schachtner, T. Zoukas, H.-D. Stachel, K. Polborn, H. Nöth, *J. Heterocycl. Chem.* **1999**, *36*, 161.
- [2] L. Ettlinger, E. Gäumann, R. Hüttler, W. Keller-Schierlein, F. Kradolfer, L. Neipp, V. Prelog, H. Zähler, *Helv. Chim. Acta* **1959**, *42*, 563; W. D. Celmer, I. A. Solomon, *J. Am. Chem. Soc.* **1955**, *77*, 2861.
- [3] S. Hamilton, G. Raymond, *Chem. Abstr.* **1984**, *101*, 189727.
- [4] H. Shiozawa, A. Shimada, S. Takahashi, *J. Antibiot.* **1997**, *50*, 449.
- [5] J. M. Webster, J. Li, G. Chen, U.S. Pat. 5,827,872, *Chem. Abstr.* **1998**, *129*, 32971a; J. M. Webster, J. Li, G. Chen, U.S. Pat. 6,020,360, *Chem. Abstr.* **2000**, *132*, 93329w; H. Hotoda, M. Kaneko, M. Inukai, Y. Muramatsu, U. Yasunori, Y. Utsui, S. Ohya, WO Pat. 2001014399, *Chem. Abstr.* **2001**, *134*, 193674.
- [6] H.-D. Stachel, J. Nienaber, T. Zoukas, *Liebigs Ann. Chem.* **1992**, 473.
- [7] J. E. Schachtner, J. Nienaber, H.-D. Stachel, K. Waissner, *Pharmazie* **1999**, *54*, 335.
- [8] H.-D. Stachel, Z. Odlerova, K. Waissner, *Collect. Czech. Chem. Commun.* **1997**, *62*, 510.
- [9] H.-D. Stachel, H. Poschenrieder, *Arch. Pharm. (Weinheim, Ger.)* **1985**, *318*, 311.
- [10] S. Oae, in 'Organic Sulfur Chemistry', Eds. F. Bernardi, I. G. Csizmadia, A. Mangini, Elsevier, Amsterdam, 1985, pp. 1–67.
- [11] H. Bock, C. Näther, A. Rauschenbach, Z. Havlas, J. W. Bats, *Phosphorus, Sulfur Silicon Relat. Elem.* **1994**, *91*, 53.
- [12] R. Mayer, *Angew. Chem.* **1957**, *69*, 481; G. V. Boyd, *Tetrahedron Lett.* **1965**, *6*, 1421; K. Hartke, D. Krampitz, *Chem. Ber.* **1974**, *107*, 739; H.-J. Timpe, A. V. El'tsov, in 'Advances in Heterocyclic Chemistry', Vol. 33, Ed. A. R. Katritzky, Academic Press, New York, 1983, p. 185; K. Hafner, B. Stowasser, V. Sturm, *Tetrahedron Lett.* **1985**, *26*, 189; O. A. Rakitin, C. W. Rees, D. J. Williams, T. Torroba, *J. Org. Chem.* **1996**, *61*, 9178.
- [13] R. Gompper, *Chem. Ber.* **1960**, *93*, 187; R. Gompper, *Chem. Ber.* **1960**, *93*, 198.
- [14] E. Immerz-Winkler, Ph.D. thesis, Universität München, 1981.
- [15] P. L. Folkin, D. N. Harpp, *J. Am. Chem. Soc.* **1991**, *113*, 8998; P. L. Folkin, D. N. Harpp, *J. Am. Chem. Soc.* **1993**, *115*, 3066; E. Perrone, M. Alpegiani, A. Bedeschi, D. Borghi, F. Giudici, G. Franceschi, *J. Org. Chem.* **1986**, *51*, 3413; F. Freeman, *Chem. Rev.* **1984**, *84*, 117.
- [16] S. Oae, T. Takata, *Tetrahedron Lett.* **1980**, *21*, 3213.
- [17] R. Wünsch, Ph.D. thesis, Univ. München, 1995.
- [18] W. E. Savage, J. Eager, J. A. Maclaren, C. M. Roxburgh, *Tetrahedron Lett.* **1964**, *5*, 3289; J. L. Kice, J. P. Cleveland, *J. Am. Chem. Soc.* **1973**, *95*, 109; E. Block, S. W. Weidman, *J. Am. Chem. Soc.* **1973**, *95*, 5046.
- [19] D. Barrilier, *Phosphorus Sulfur Relat. Elem.* **1980**, *8*, 79; C. Reichardt, *Angew. Chem., Int. Ed.* **1979**, *18*, 98; C. Reichardt, 'Solvents and Solvent Effects in Organic Chemistry', VCH, Weinheim, 1988; F. Effenberger, F. Würthner, *Angew. Chem.* **1993**, *105*, 742.
- [20] W. Weigand, G. Bosl, C. Robl, W. Amrein, *Chem. Ber.* **1992**, *125*, 1047.
- [21] W. Weigand, G. Bosl, B. von Dielingen, K. Gollnick, *Z. Naturforsch., B* **1994**, *49*, 513.

- [22] R. Wünsch, G. Bosl, W. Weigand, *J. Organomet. Chem.* **2001**, 621, 352.
- [23] P. C. B. Page, S. S. Klair, M. P. Brown, M. M. Harding, C. S. Smith, S. J. Maginn, S. Mulley, *Tetrahedron Lett.* **1988**, 29, 4477; P. C. B. Page, S. S. Klair, M. P. Brown, C. S. Smith, S. J. Maginn, S. Mulley, *Tetrahedron* **1992**, 48, 5933.
- [24] W. Weigand, R. Wünsch, *Chem. Ber.* **1996**, 129, 1409.
- [25] A. Shaver, P. Y. Plouffe, *J. Am. Chem. Soc.* **1991**, 113, 7780; M. El-khateeb, B. Wolfsberger, W. A. Schenk, *J. Organomet. Chem.* **2000**, 612, 14; M. El-khateeb, A. Shaver, A.-M. Lebuis, *J. Organomet. Chem.* **2001**, 622, 293.
- [26] A. Shaver, H. Boily, A.-M. Lebuis, *Inorg. Chem.* **1996**, 35, 6356.
- [27] M. Hernández, G. Miralrio, A. Arévalo, S. Bernès, J. J. García, C. López, P. M. Maitlis, F. del Rio, *Organometallics* **2001**, 20, 4061.
- [28] U. Nagel, *Chem. Ber.* **1982**, 115, 1998.

Received June 20, 2002