Synthesis and Reactions of New Dithiolopyrroles[1][2])

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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 dithiolopyrrole **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 $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ (**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 Pt^0 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-dithiolopyrrolones of general formula **3** [1][6][7]. Some of these compounds exhibited pharmacologically valuable activities [8]. Supposedly, *S*-oxides of the respective dithiolopyrrolones play a decisive role in the physiological activity [1]. It was shown that pyrrothins and other 1,2-dithiolopyrroles 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 dithiolopyrrolones **3**, which we assumed to be more stable against alkali.

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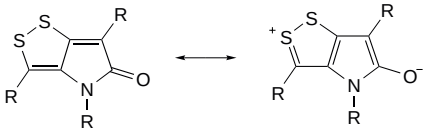
[1]) Fused 1,2-Dithioles, Part VI.

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



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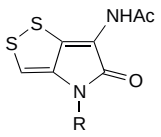

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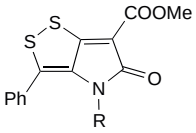

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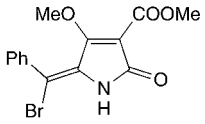
Results and Discussion. – The synthesis started from the known lactam **4** [9]. Upon reaction with Na_2S, nucleophilic displacement first of the MeO group and then of Br occurred to yield a red dithiolate. The salt could not be isolated as an analytically pure substance because of its ready oxidation by O_2 in air. After completing the oxidation with oxidants like I_2 or H_2O_2, the dithiole **5a** was obtained in good yield. The disulfide bond of **5a** was reduced with $NaBH_4$ to the red dithiolate, which, upon re-oxidation, gave back **5a** quantitatively.



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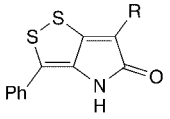
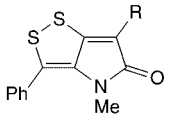
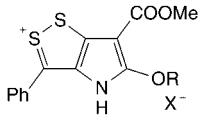


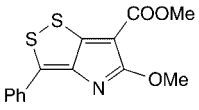
5a R = COOMe
b R = COOH
c R = H
d R = NO
e R = NH_2
f R = NHAc



6a R = COOMe
b R = COOH
c R = H
d R = NO
e R = NH_2
f R = NHAc
g R = COCl
h R = CON_3
i R = Ac
j R = C(Me)NOH



7 R = H, X = ClO_4
8 R = Me, X = FSO_3



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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].

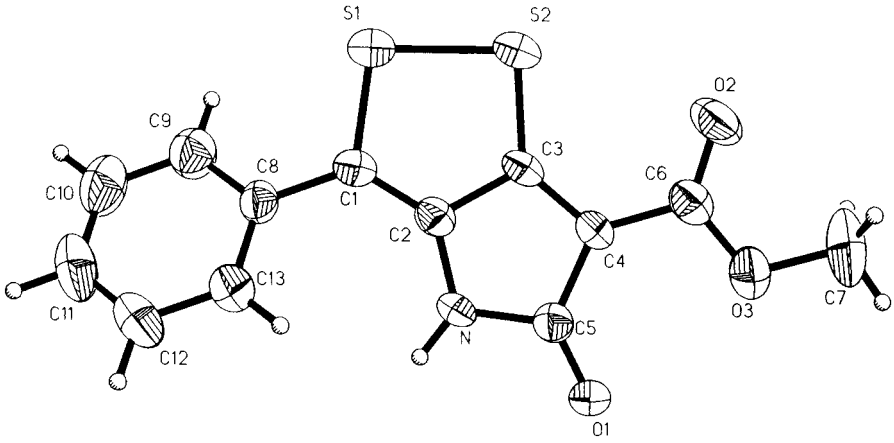

Fig. 1. *Molecular structure of* **5a** *in the crystal*

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 possibity 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, HNO_2 gave the green nitroso derivatives **5d**/**6d**, which also could be obtained directly from the acids **5b**/**6b** upon heating with $NaNO_2$ to 40°. Compounds **5d**/**6d** were reduced with $NaBH_4$ 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 dithiolopyrrolidone **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 dithiolopyrrolones 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, noteworthily, 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 pyrrothin *S*-oxides [1] as well as from acyclic representatives [18]. MS of the thiosulfinates showed M^+ as well as $[M-O]^+$ peaks. MS of the dioxides **10b**/**11b** gave evidence of another route of decomposition by $[M-SO_2]^+$ fragments beside the molecular-ion peaks. The most prominent peak in the

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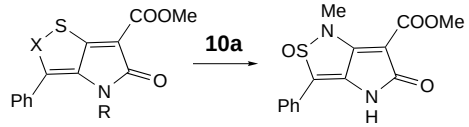
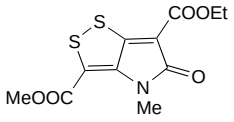
[3]) The term 'pseudoazulene' was frequently used for cyclopenta[1,2]dithioles.

Scheme



10a R = H, X = SO
b R = H, X = SO_2
11a R = Me, X = SO
b R = Me, X = SO_2

12



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

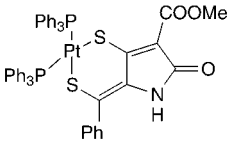
The chemical behavior of the *S*-oxides **10**/**11** is characterized by a bicyclic system that is less stable against alkali in comparison with the dithioles **5**/**6**. As already mentioned, the *S*-oxide **10a** rapidly suffered cleavage of the dithiolo ring with an amine, while the dithiolopyrrole **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 dithiolopyrrole **5a** could be recovered unchanged from the aqueous solutions of its potassium salt after 3 d. The oxides **10a**/**b** were converted by CH_2N_2 to the *N*-methylated derivatives **11a**/**b** exclusively, while the reaction of **5a** with CH_2N_2 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 wavelenghts, 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 dithiole **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 thiosulfinates react readily with Pt^0 complexes $[Pt(\eta^2\text{-}C_2H_4)(PR_3)_2]$ *via* insertion of Pt^0 into the S–S(O) bond, to give chelate complexes containing sulfenato-thiolato compounds. Thus, we studied the oxidative addition of Pt^0 compounds with the thiosulfinate **10a**. We also extended the study of reactivity of $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ (**14**) toward the disulfides **5a** and **13**, respectively, as well as the thiosulfonate **10b**.

$[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$

14



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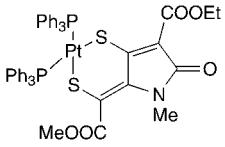

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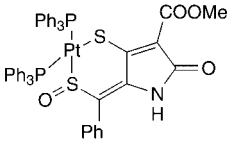

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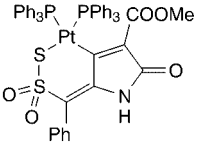

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Reaction of a mixture of **14** and **5a** in toluene at room temperature under N_2 afforded the dithiolato complex **15** after workup. The analogous complex **16** was also formed *via* insertion of Pt^0 into the S–S bond of **13**.

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(Pt,P) = 2927, 2939 Hz, ^2J(P,P) = 31.5 Hz; **15**) and δ 22.48, 22.76 ppm (^1J(Pt,P) = 2956, 3012 Hz, ^2J(P–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(C,P) = 5.6 Hz) and 141.2 ppm (^3J(C,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(Pt,P) = 2280 Hz, ^2J(P,P) = 30.5 Hz), for P *trans* to S(O), and δ 22.04 ppm [^1J(Pt,P) = 3435 Hz, ^2J(P,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

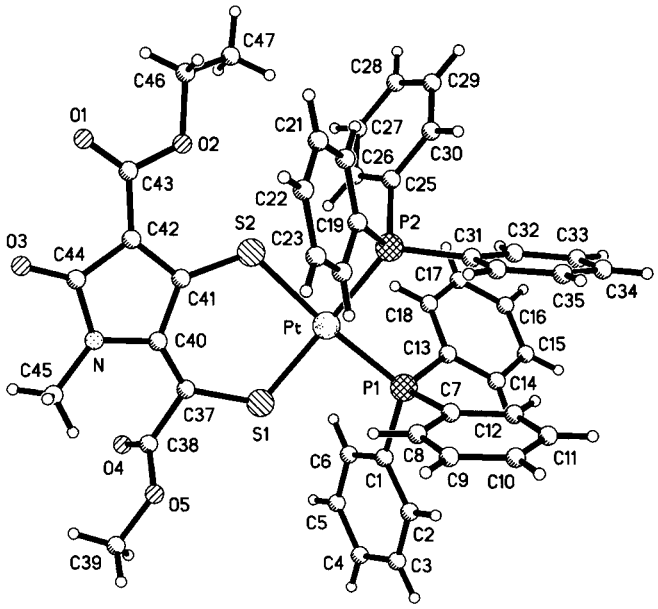

Fig. 2. *Molecular structure of* **16** *in the crystal*

Table 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 $\tilde{\nu}$(SO) band at 999 cm^{-1}, which is in agreement with these absorptions observed for other sulfenato complexes [22]. The $\tilde{\nu}$(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 $R'-S-SO_2-R$ are known, metal complexes containing the anion $R-SO_2-S^-$ as ligands are very rare and limited to few Fe(II) as well as Ru(II) complexes like $[M(S-SO_2R)(C)L_2]$ (M = Fe, Ru) [25]. The $R-SO_2-S^-$ ligands are isomeric with those in *trans*-[Pt(phthalimido)-

$(SO_2-S-R)](PPh_3)_2$ [26]. Complex **18** was characterized by spectroscopic methods and by X-ray structure determination (*Fig. 3*). Both methods confirmed that insertion of Pt(0) takes place selectively into the C–S bond in the case of thiosulfonate **10b**, yielding the Pt bonded thiosulfonato complex. The ^{31}P-NMR spectrum of **18** exhibited the coupling pattern of an *AB* spin system; it confirmed that the *trans* influence of the *C*-donor atom is stronger than that of the *S*-donor atom: δ 7.47 (^1J(Pt,P) = 2054 Hz, ^2J(P,P) = 20.7 Hz; P *trans* to C) and δ 12.56 ppm (^1J(Pt,P) = 3724 Hz, ^2J(P,P) = 20.7 Hz; P *trans* to S) [27]. The significant bands in the IR spectrum of complex **18** are those associated with the thiosulfonyl group, which shows both symmetric (1273 cm^{-1}) and asymmetric modes (1094 cm^{-1}), respectively [25]. These bands are shifted to lower wavenumbers compared to those of the parent thiosulfonate **10b** (1342, 1145 cm^{-1}) due to the electron-donating effect of the electropositive Pt-atom.

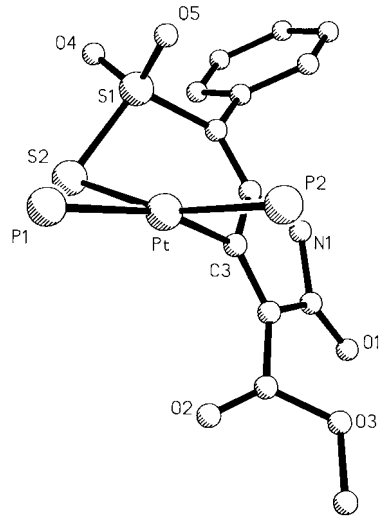

Fig. 3. *Molecular structure of* **18** *in the crystal*. The phenyl rings at the P-atoms have been omitted for clarity.

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 Ph_3P 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 Anacomp-220* or *Perkin-Elmer Lambda-20*; λ_{max} in nm (log ε) in MeOH soln., if not stated otherwise. ^{1}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 (*GP A*). *Synthesis of Thiosulfinates from Dithioles.* A soln. of 0.27 g (1.1 mmol) of *m*CPBA (70%) in CH_2Cl_2 (10 ml) was added to a stirred soln. of the dithiole (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 (*GP B*). *Synthesis of Thiosulfonates from Dithioles.* A soln. of 0.52 g (2.1 mmol) of *m*CPBA (70%) in CH_2Cl_2 (10 ml) was added to a stirred soln. of the dithiole (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 (*GP C*). *Reduction of Thiosulfinates with 1,2-Dimethylhydrazine.* A soln. of the dithiole *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 anh. 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 $Na_2S \cdot 9\,H_2O$ 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-1*H*-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, 1728*s*, 1685*s*, 1660*s*. ^{1}H-NMR: 11.16 (*s*, 1 H); 7.66 (*m*, 5 H); 3.81 (*s*, 3 H). MS: 291 (M^+), 121. Anal. calc. for $C_{13}H_9NO_3S_2$ (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}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 $C_{12}H_7NO_3S_2$ (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(4*H*)-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 CO_2 had ceased, the mixture was cooled, diluted with CH_2Cl_2 (20 ml), filtered, and concentrated *in vacuo*. Upon addition of Et_2O, the product started to crystallize. 55% of **5c**. Orange crystals. M.p. 215–216° (Et_2O). UV: 376 (4.196), 261 (3.915). IR: 3130, 2990, 1670. ^{1}H-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 $C_{11}H_7NOS_2$ (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(4*H*)-one* (**5d**). An aq. soln. of 0.70 g (10 mmol) of $NaNO_2$ 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. ^{1}H-NMR: 11.52 (*s*, 1 H); 7.97–7.50 (*m*, 5 H). MS: 262 (M^+), 121. Anal. calc. for $C_{11}H_6N_2O_2S_2$ (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(4*H*)-one* (**5e**). A soln. of 0.26 g (1 mmol) of **5d** and 0.38 g (10 mmol) of $NaBH_4$ 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. ^{1}H-NMR: 7.58–7.30 (*m*, 5 H); 4.30 (*m*, 3 H). MS: 248 (M^+), 121. Anal. calc. for $C_{11}H_8N_2OS_2$ (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 Ac_2O (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/CH_2Cl_2 1:1). UV: 415 (4.141), 322 (3.829), 259 (4.237). IR: 3230, 3160, 3020, 1650, 1635, 1600. ^{1}H-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 $C_{13}H_{10}N_2O_2S_2$ (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 CH_2Cl_2 (30 ml) and extracted three times with H_2O. The org. layer was dried (Na_2SO_4) 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. ^{1}H-NMR: 7.62 (*s*, 5 H); 3.80 (*s*, 3 H); 2.88 (*s*, 3 H). MS: 305 (M^+), 121. Anal. calc. for $C_{14}H_{11}NO_3S_2$ (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. ^{1}H-NMR: 12.2 (br. *s*, 1 H); 7.6 (*s*, 5 H); 2.90 (*s*, 3 H). MS: 291 (M^+), 121. Anal. calc. for $C_{13}H_9NO_3S_2$ (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(4*H*)-one* (**6c**). As described for **5c**, with 0.87 g (3 mmol) of **6b**. The residue was purified by FC (1. petrol ether, 2. Et_2O). The second fraction was collected, and the solvent was removed *in vacuo*. 51% of **6c**. Orange crystals. M.p. 137–138° (Et_2O). UV: 366 (4.271), 244 (sh), 219 (4.018). IR: 3100, 2920, 1655. ^{1}H-NMR: 7.56 (*s*, 5 H); 6.03 (*s*, 1 H); 2.86 (*s*, 3 H). ^{1}H-NMR ($CDCl_3$): 7.48 (*s*, 5 H); 5.97 (*s*, 1 H); 3.00 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 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 $C_{12}H_9NOS_2$ (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(4*H*)-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. ^{1}H-NMR: 7.93 (*s*, 5 H); 3.10 (*s*, 3 H). MS: 275 ($[M-1]^+$), 121. Anal. calc. for $C_{12}H_8N_2O_2S_2$ (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(4*H*)-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. ^{1}H-NMR: 7.47 (*s*, 5 H); 2.83 (*s*, 3 H). MS: 262 (M^+), 121. Anal. calc. for $C_{12}H_{10}N_2OS_2$ (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 PCl_5 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. $NaHCO_3$ 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° (EtOH). UV: 394 (4.091), 314 (3.919), 252 (4.273). IR: 3260, 3040, 2920, 1670, 1645, 1600. ^{1}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. Anal. calc. for $C_{14}H_{12}N_2O_2S_2$ (304.39): C 55.24, H 3.97, N 9.20, S 21.07; found: C 55.24, H 3.90, N 9.05, S 20.93.

*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°. UV: 386 (4.198), 220 (4.023). IR: 2940, 1780, 1765, 1660. MS: 282 ([$M-28$]$^+$), 121. Anal. calc. for $C_{13}H_8ClNO_2S_2$ (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-penyl[1,2]dithiolo[4,3-*b*]pyrrol-5(4*H*)-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° (acetone/H_2O 1:1). UV: 415 (4.298), 248 (4.102). IR: 3050, 2940, 2130, 1705, 1670, 1645, 1600. ^{1}H-NMR: 7.67 (*s*, 5 H); 2.93 (*s*, 3 H). MS: 288 ([$M-28$]$^+$), 121. Anal. calc. for $C_{13}H_8N_4O_2S_2$ (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(4*H*)-one* (**6i**). To a suspension of 0.14 g (1 mmol) of powdered anh. $AlCl_3$ in anh. 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° (MeOH). UV: 413 (4.115), 263 (3.761), 225 (4.288). IR: 3050, 2940, 1665, 1600. ^{1}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 $C_{14}H_{11}NO_2S_2$ (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(4*H*)-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° (MeOH). UV: 412 (3.960), 344 (3.877), 258 (4.278). IR: 3260, 1645, 1600. ^{1}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 $C_{14}H_{12}N_2O_2S_4$ (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-4*H*-[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° (dec.). UV ($HClO_4$): 368 (3.970), 285 (3.807), 243 (4.001). IR: 3340 (br.), 3240, 3040, 2920, 2830, 1710, 1660, 1590. ^{1}H-NMR: 11.08 (*s*, 1 H); 7.55 (*s*, 5 H); 3.81 (*s*, 3 H).

*5-Methoxy-6-(methoxycarbonyl)-3-phenyl-4*H*-[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 anh. 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° (MeOH). UV: 381 (4.311), 293 (sh), 247 (3.872), 215 (4.165). IR: 3040, 2990, 1717, 1670. ^{1}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 $C_{14}H_{11}NO_3S_2$ (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-2*H*-2*λ^4*-[1,2]dithiolo[4,3-*b*]pyrrole-6-carboxylate* (**10a**). According to *GP A*, with 0.58 g (2 mmol) of **5a**. 46% of **10a**. Faintly yellow crystals. M.p. 226–228° (AcOH). UV: 329

(4.210), 226 (4.120). IR: 3280, 3150, 3056, 2957, 1758, 1714, 1655, 1071. ^{1}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 $C_{13}H_9NO_4S_2$ (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-2 H-2λ⁶-[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 anh. 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}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 $C_{13}H_9NO_5S_2$ (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-2*H*-2λ⁴-[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}H-NMR: 7.63 (*s*, 5 H); 3.86 (*s*, 3 H); 2.75 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 167.2 (C(5)); 163.1 (*C*OOMe); 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 $C_{14}H_{11}NO_4S_2$ (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-2*H*-2λ⁶-[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}H-NMR ($CDCl_3$): 7.60 (*s*, 5 H); 3.98 (*s*, 3 H); 2.90 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 165.2 (C(5)); 162.5 (*C*OOMe); 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 $C_{14}H_{11}NO_5S_2$ (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-2λ⁴-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}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 $C_{14}H_{12}N_2O_4S$ (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 [Pt(η²-C₂H₄)(PPh₃)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: 3100*w*, 1714*s*, 1685*s*, 1655 (br.). ^{1}H-NMR (CD_2Cl_2): 7.00–7.42 (*m*, 35 arom. H); 6.95 (*s*, NH); 3.37 (*s*, Me). ^{13}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}P-NMR (CH_2Cl_2): 21.08, 21.49 (^1J(Pt,P) = 2939, 2927, ^2J(P,P) = 31.5). Anal. calc. for $C_{49}H_{39}NO_3P_2PtS_2$ (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: 3070*w*, 2964*m*, 1711*s*, 1651*s*. ^{1}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*, $J=7.1$, *Me*CH_2). ^{31}P-NMR (CH_2Cl_2): 19.76, 22.07 (^1J(Pt,P) = 3010, 2951, ^2J(P,P) = 31.3). Anal. calc. for $C_{47}H_{41}NO_5P_2PtS_2$ (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: 3441*w*, 3051*w*, 1721*s*, 1709*s* (sh), 999*m*. ^{1}H-NMR (CD_2Cl_2): 7.00–7.55 (*m*, 35 arom. H); 6.73 (*s*, NH); 3.53 (*s*, Me). ^{13}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(Pt,P) = 2280, 3435, ^2J(P,P) = 30.5). Anal. calc. for $C_{49}H_{39}NO_4P_2PtS_2$ (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: 3443*m*, 3018*m*, 1717*s*, 1706*s*, 1628*m*, 1273*s*, 1094*s*. ^{1}H-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	$C_{13}H_9NO_3S_2$	$C_{47}H_{41}NO_5P_2PtS_2$	$C_{49}H_{39}NO_5P_2PtS_2 \cdot 2.12\ H_2O$
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	*I*2/*a* (no. 15)	$P\bar{1}$	*P*2/*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
$\lvert F \rvert > 3\sigma_{\lvert F \rvert}$	1486		7153
$I > 2\sigma_I$		6461	
Quantity minimized	$\Sigma(\lvert F_o \rvert - \lvert F_c \rvert)^2$	$\Sigma(\lvert F_o \rvert^2 - \lvert F_c \rvert^2)^2$	$\Sigma(\lvert F_o \rvert - \lvert F_c \rvert)^2$
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 [e · Å^{-3}]	+0.42/−0.38	+0.89/−0.87	+0.91/−1.60

[a]) $R = \Sigma \lvert\lvert F_o \rvert - \lvert F_c \rvert\rvert / \Sigma \lvert F_o \rvert$. [b]) $wR = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / \Sigma w \lvert F_o \rvert^2]^{1/2}$ and the $\lvert F \rvert^2$ equiv., resp. [c]) $s = \Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2/(N - N_P)$ with N = number of reflections, N_P = number of parameters; and the $\lvert F \rvert^2$ 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(Pt,P) = 2054, 3724, ^2J(P,P) = 20.7). Anal. calc. for $C_{49}H_{39}NO_5P_2PtS_2$ (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.uk).

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

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Received June 20, 2002