Functionalized 1,1-Ethene Dithiolates as Ligands, V [1]. Synthesis and Crystal Structure of Palladium(II) and Platinum(II) Complexes with Dithioylidene Barbituric Acid Ligands. Molecular Structure of a 2,6-Diaminopyridine-Platinum(II) Barbiturate Complex

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Dedicated to Professor Dr. Dr. h. c. Dieter Seebach on the occasion of his 60th birthday

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Intermolecular Hydrogen-Bonding, Supramolecular Self-Assembly, Dithioylidene Barbituric Acid, Palladium Complex, Platinum complexes

The 1,1-ethene dithiolato ligands (dithioylidene barbituric acids) **2a**-**f** react with palladium(II) and platinum(II) compounds L_2MCl_2 [M = Pd, Pt; L = PEt₃, PBu₃, PPh₃, 1/2 dppe, 1/2 (-)-DIOP, 1/2 2,9-dimethyl phenanthroline] to give the 1,1-ethene dithiolato metal complexes $L_2M[S_2C=C-C(O)-NR^1-C(O)-NR^2-C(O)]$ **3**-**7**. Compound **4a** forms a 1:1 adduct (**8**) with 2,6-diaminopyridine. The compounds were characterised on the basis of their IR and NMR (¹H, ¹³C, ³¹P) spectra. Complexes **4a**, **4c**, and **5a** were further studied by X-ray structural analysis. The barbituric unit in **4a** undergoes self-assembly through multiple hydrogen-bonding with complementary 2,6-diaminopyridine yielding the supramolecular complex **8**.

Introduction

The reactions of ketones as well as of other active methylene compounds with carbon disulfide in the presence of a base yielding the 1,1-ethene dithiolates are known since 1891 [2]. There is currently a growing interest in the preparation of metal complexes containing functional 1,1-ethene dithiolato ligands which allow the synthesis of heterodi- and -trimetallic compounds [3], complexes exhibiting fluorescence [4] as well as amphihilic and metallomesogenic [5]. The occurrence of such properties is usually achieved by subtle changes in the specific functionalities of a given ligand system.

Barbituric acid is also readily converted into the 1,1-ethene dithiolate by carbon disulfide in the presence of triethylamine. Its derivatives have attracted considerable interest as models for molecular selfassembly processes as shown by Lehn *et al.* [6], Whitesides *et al.* [7], Hamilton *et al.* [8], and others [9]. However, little is known about the coordination chemistry of these biologically important ligands.

Barbituric acid and its derivatives can coordinate through one or both of their deprotonated nitrogen atoms, and the carbonyl oxygen atoms, and the parent barbituric acid through the deprotonated methylene group giving access to a wide range of metal complexes. So far, most studies have concentrated on the first-row Transition Metals [10], and relatively few experiments are reported for platinum group metals [11] or copper, silver, gold and zinc [12]. Very recently platinum(II) complexes of 5,5diethyl barbituric acid containing ancillary phosphane ligands have been prepared [13]. A number of transition metal complexes of related ligands such as orotic acid, 5-aminoorotic acid, and 5-(2-pyridyl methylene)hydantoin have been reported by Mingos et al. [14].

We aimed at a synthesis of palladium(II) and platinum(II) complexes with 1,1-ethene dithiolato derivatives of barbituric acid (dithioylidene barbituric acids) as ligands. These compounds should

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[#] Crystal structure determination.



be able to form two or three strong intermolecular hydrogen bonds particularly with a complementary base like 2,6-diamino pyridine.

Results and Discussions

The 1,1-ethene dithiolates $2\mathbf{a} \cdot \mathbf{f}$ have been prepared in a one-step synthesis by treating a DMSO solution of the barbituric acids $1\mathbf{a} \cdot \mathbf{c}$ with carbon disulfide in the presence of triethylamine at room temperature [15]. The reactions between the resulting orange suspensions with (Ph₃P)₂PdCl₂ and the platinum(II) complexes L₂PtCl₂ [L = PEt₃, PBu₃, PPh₃, 1/2 dppe, 1/2 (-)-DIOP], respectively, proceed smoothly in DMSO at room temperature to give the metal complexes **3** · **6** as yellow air-stable microcrystalline solids in good yields. Complexes **3**, **4a** - **c**, **5a**, **b**, and **6a**, **c** are isolated by recrystallisation from a mixture of dichloromethane / hexane or by chromatography.

The IR spectra show three (3-5d, 7) or two (6a-c) intense bands, respectively, in the range of



1625 - 1716 cm⁻¹ assigned to the non-equivalent carbonyl groups. ν (NH) bands are detected at 3030 - 3435 cm⁻¹ for the *N*,*N'*-unsubstituted as well as the *N*-monosubstituted complexes, which indicate the presence of strong hydrogen-bonds of type NH···O=C [16].

The ³¹P{¹H} NMR spectra of the platinum complexes **4a-d** and **6a-c** show singlets with ¹⁹⁵Pt satellites indicating the presence of two equivalent phosphorus atoms. In contrast, the ³¹P{¹H} NMR spectra of the *N*-monosubstituted complexes **5a-d** exhibit AB spin patterns for two chemically nonequivalent phosphorus atoms. The coupling constants ¹J(¹⁹⁵Pt-³¹P) are rather similar to each other.

The ¹H NMR spectra of **3 - 5d** and **7** show in each case one resonance due to the NH protons. The chemical shifts of these protons are concentration dependent in CDCl₃ or CD₂Cl₂ suggesting hydrogen-bond interactions between the barbituric acid fragments.

In the ¹³C{¹H} NMR spectra of **4a**, **5b**, **c**, and **6c** the S₂*C*=C resonances appear between 216 and



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Fig. 1. Part of the hydrogen-bonded zig-zag chain formed by 4a; for the sake of clarity the hydrogen atoms at the phosphine ligands have been omitted. Selected atom distances [pm] and bond angles [°]: Pt(1)-S(1) 234.6(2), Pt(1)- $S(2)^{2}34.1(2), Pt(1)-P(1) 228.2(3), Pt(1)-P(2) 227.8(2), S(1)-C(1) 174.0(9), S(2)-C(1) 173.2(8), C(1)-C(2) 140.0, Pt(1)-Pt(2) 227.8(2), Pt(1)-Pt(1)-Pt(2) 227.8(2), Pt(1)-$ N(6b)···O(5c) 283, N(4e)···O(3a) 280; P(1)-Pt(1)-P(2) 101.86(9), S(1)-Pt(1)-S(2) 73.59(8), S(1)-C(1)-S(2) 107.9(5), S(1)-C(1)-C(2) 125.9(7), S(2)-C(1)-C(2) 126.2(7).



Fig. 2. Molecular structure of $4c \cdot 2$ DMSO; for the sake of clarity the hydrogen atoms at the phosphine ligands have been omitted. Selected atom distances [pm] and bond angles $[^{\circ}]$: Pt(1)-S(1) 234.12 (9), Pt(1)-S(2) 234.54 (9), Pt(1)-P(1) 227.30 (9), Pt(1)-P(2) 226.52 (9), S(1)-C(1) 175.3 (4), S(2)-C(1) 174.4 (3), C(1)-C(2) 138.6 (5), S(20)-O(20) 149.5 (3), S(30)-O(30) 151.1 (3), N(2)····O(20) 276, N(1)…O(30) 285; P(1)-Pt(1)-P(2) 85.80 (3), S(1)-Pt(1)-S(2) 73.99 (3), S(1)-C(1)-S(2) 107.9 (5), S(1)-C(1)-C(2) 126.0 (3),

220 ppm; in the case of 5a a three-bond coupling to the tributylphosphane phosphorus atom (3.5 Hz) and a two-bond coupling to the 195 Pt isotope (79.3 Hz) are resolvable. The 13 C NMR resonances

of the quaternary $S_2C=C$ carbon atom appear for 4a and **5a**, **c** at $\delta \sim 108$ with ¹⁹⁵Pt satellites. Complexes 4a and 6c show the expected two, and complexes 5a, c three carbonyl ¹³C NMR resonances.



Molecular Structures of 4a, 4c, 5a and 8

The molecular structure of complexes 4a, $4c \cdot 2$ DMSO, 5a and 8 are depicted in Figs. 1 - 4 and bond lengths and angles in the captions to the figures. Compounds 4a, 4c and 5a crystallise from a mixture of dichloromethane / DMSO [8:1] at 0°C.

The crystal structure of 5a (Fig. 3) confirms that **1b** is acting as a bidendate dianionic ligand. The molecules 5a form centrosymmetrical dimers via two equivalent N(6)-H \cdots O(5) hydrogen bonds; the N(6)O(5) distance is 294 pm. The platinum(II) ion resides in a square-planar environment. The planes Pt(1)P(1)P(2) and Pt(1)S(1)S(2) include an angle of 5.4° . The plane Pt(1)S(1)S(2)C(1) and the barbituric acid moiety are slightly tilted with respect to each other, the interplanar angle being 12.3°. The two Pt-S bonds are of equal lengths [233.6(3) and 233.8(3) pm]; comparable values are found in $(Ph_3P)_2Pt[S_2C=CH-C(O)Ph]$ [4g] and $(Ph_3P)_2Pt[S_2C=CH-C(O)(C_5H_4)Fe(C_5H_5)][3]$. The intramolecular $S(1) \cdots S(2)$ distance (280.4 pm) is significantly shorter than the sum of the van der Waals radii; this corres-ponds with data for other 1,1-ethene dithiolato platinum(II) complexes [3, 4g].

The molecular structure of **4a** (Fig. 1) reveals a zig-zag like polymeric motif. A folded ribbon is formed by a continuous array of the barbituric acid units, each of which is linked via pairs of N-H···O hydrogen bonds between the imido N-H atoms and the carbonyl O atoms [N(6)-H···O(5) / N(4)-H···O(3)]. The distance between N(6b) and O(5e) as well as O(5b) and N(6e), respectively is 73.1 pm. The hydrogen-bonding distances between the barbituric acid ligands indicate strong interactions: N(6)···O(5) 283 pm, N(4)···O(3) 280 pm. Fig. 3. Hydrogen-bonded dimers of complex **5a**; for the sake of clarity the butyl groups at the phosphines have been omitted. Selected atom distances [pm] and bond angles [$^{\circ}$]: Pt(1)-S(1) 233.6 (3), Pt(1)-S(2) 233.8 (3), Pt(1)-P(1) 227.7 (3), Pt(1)-P(2) 227.4 (3), S(1)-C(1) 172.1 (10), S(2)-C(1) 172.8 (9), C(1)-C(2) 140.6 (12), N(6)-··O(5) 294; P(1)-Pt(1)-P(2) 101.24 (9), S(1)-Pt(1)-S(2) 73.81 (8), S(1)-C(1)-S(2) 108.8 (5), S(1)-C(1)-C(2) 124.4(7), S(2)-C(1)-C(2) 126.6 (7).



Fig. 4. Molecular structure of **8**; the hydrogen-bonded adduct formed between **4a** and 2,6-diaminopyridine; for the sake of clarity the ethyl groups at the phosphines have been omitted. Selected atom distances [pm] and bond angles [°]: Pt(1)-S(1) 233.3(6), Pt(1)-S(2) 234.0(4), Pt(1)-P(1) 228.3(6), Pt(1)-P(2) 227.9(6), S(1)-C(13) 171(2), S(2)-C(13) 170(2), C(13)-C(14) 144(3), N(1a)···O(2b) 287, N(3a)···O(2a) 300, N(2a)···N(5a) 286, N(4a)···O(3a) 306; P(1)-Pt(1)-P(2) 100.2(2), S(1)-Pt(1)-S(2) 73.4(2), S(1)-C(13)-S(2) 110.0(11), S(1)-C(13)-C(14) 125.0(14), S(2)-C(1)-C(2) 124.6(14).

Contrary to 5,5-diethylbarbituric acid which forms six different polymorphs [17], **4a** does not show polymorphism. Further hydrogen-bonding modes leading to poly-morphism are prevented in **4a** by the bisphosphine platinum(II) complex fragment which is acting as a blocking group [14a, e].

Unlike 4a and 5a the molecular structure of compound 4c (Fig. 2) shows that in this complex the barbituric acid units are not interconnected by hydrogen-bonds. The reason seems to be the sterically demanding dppe ligand. However, hydrogen-bonds are formed between the N-H and the O=S

groups of the smaller, solvate DMSO molecules (vide supra) [N(1) \cdots O(30) 285 pm, N(2) \cdots O(20) 276 pm].

Suitable single co-crystals of 8 (Fig. 4) were obtained from a dichloromethane solution containing equimolar amounts of 4a and 2.6-diaminopyridine at room temperature. Each molecule of 4a is linked to a 2,6-diaminopyridine molecule via three hydrogen-bonds – one shorter $[N(2) \cdots N(5) 286 \text{ pm}]$ and two longer [N(3)...O(2) 300 pm, N(4)...O(3) 306 pm] linkages. The weakness of the two interactions $N(3)\cdots O(2)$ as well as $N(4)\cdots O(3)$ is a consequence of the non-coplanarity of the barbituric acid unit and the 2,6-diaminopyridine ring which are tilted by 36° with respect to each other. These 1+1 adducts are associated into 2+2 dimers through two strong hydrogen-bonds between the amido protons N(1)-H and the carbonyl O(2) atoms $[N(1)\cdots O(2) 287]$ pm]. Further oligomerisation of the 2+2 adducts is prevented by the bisphosphine platinum(II) complex fragment. A similar hydrogen-bonding motif has been observed between platinum(II) orotate and 2,6-diaminopyridine [14d].

Experimental

DMSO, barbituric acid (1a) and 2,6-Dry diaminopyridine were purchased from Fluka. N-Methyl barbituric acid (1b) [18], N-hexyl barbituric acid (1c) [18], N-dodecyl barbituric acid (1d) [18], N,N'-dimethyl barbituric acid (1e) [19], N,N'-dibenzyl barbituric acid (1f) [19] as well as the complexes $(Bu_3P)_2PdCl_2$ [20], $(Et_3P)_2PtCl_2[21], (Bu_3P)_2PtCl_2[20], (Ph_3P)_2PtCl_2[20],$ (dppe)PtCl₂[22], [(-)-DIOP]PtCl₂[22] and (2,9-dimethylphenanthroline)PtCl₂ [23] were prepared according or analogously to literature procedures. Chromatography: Kieselgel 60 (Merck); column length: 40 cm, column diameter: 4 cm. - IR: Perkin-Elmer 841, Nicolet 520. -NMR: JEOL GSX 270 (109.37 MHz for ³¹P; H₃PO₄ as external standard), JEOL EX 400 (399.78 and 100.53 MHz, for ¹H and ¹³C, respectively). For ¹H and ¹³C NMR TMS was used as an internal standard. - Elemental analyses: Heraeus VT. - Melting and decomposition points (uncorrected): Electrothermal Digital Melting-Point-Apparatus.

General procedure for compounds 2a - f

To solutions of 10 mmol of 1a - f in 10 ml of DMSO were added triethylamine (2.80 ml, 20 mmol) and carbon disulfide (0.6 ml, 10 mmol). The solutions were stirred for 2 h at r. t. During this period they turned orange. These stock solutions were used for further experiments.

Preparation of 3

At r. t. a mixture of 0.8 mmol (1 ml of the DMSO stock solution) of 2c was added to a solution of 0.29 g (0.5 mmol) of (Bu₃P)₂PdCl₂ in 10 ml of DMSO. The orangevellow mixture was stirred for 2 d at r. t. After addition of 10 ml of water the suspension was extracted with three 20-ml portions of dichloromethane. The combined organic extracts were washed with 20 ml of water and dried with sodium sulfate. The solvent was removed in vacuo, and the resulting orange residue was purified by column chromatography using hexane/ethyl acetate (2:1) as the eluent. The main orange-yellow fraction, eluted first, was collected and the solvent was removed in vacuo. Orange powder. - Yield 0.24 g (59%), m. p. > 250 °C (dec.). -IR (KBr): $\nu = 3432 \text{ cm}^{-1}$ (w, br), 3184 (m), 3065 (m) (OH/NH), 1700 (s), 1673 (s), 1635 (s) (C=O), 1462 (s), 1392 (vs, br) (C=C/C=O). - ¹H NMR (JEOL FX 90-O, 90 MHz, CDCl₃): δ = 3.81 (m, 2H, NCH₂), 8.89 (br. s, 1H, NH). - ³¹P NMR (JEOL FX 90-Q, 36.21 MHz, CH₂Cl₂): $\delta = 8.0.$

 $\begin{array}{l} C_{35}H_{68}N_2O_3P_2PdS_2 \ (M=797.4 \ g/mol)\\ Calcd \ C \ 52.72 \ H \ 8.59 \ N \ 3.51 \ S \ 8.04 \ \%,\\ Found \ C \ 52.79 \ H \ 8.33 \ N \ 3.54 \ S \ 8.70 \ \%. \end{array}$

4a was prepared from 0.8 mmol (1 ml of the DMSO stock solution) of **2a** and 0.25 g (0.5 mmol) of $(Et_3P)_2PtCl_2$ in 10 ml of DMSO (reaction time: 2 d, colour: bright-yellow) and the product was purified as described for **3**. Yellow powder. – Yield 0.21 g (67 %), m. p. > 250 °C (dec.). – IR (KBr): ν = 3436 cm⁻¹ (w, br), 3194 (m), 3033 (w) (OH/NH), 1748 (m), 1710 (s), 1676 (s), 1635 (s) (C=O), 1451 (s), 1401 (vs, br) (C=C/C=O). – ¹H NMR (CD₂Cl₂): δ = 7.86 (br. s, 2H, NH). – ¹³C NMR (CD₂Cl₂): δ = 107.34 (s, S₂C=C), 149.44, 161.70 (s, C=O), 220.81 (s, S₂C =C). – ³¹P NMR (CD₂Cl₂): δ = 4.78 (s, ¹J(¹⁹⁵Pt-³¹P) = 2862 Hz).

 $\begin{array}{l} C_{17}H_{32}N_2O_3P_2PtS_2 \ (M=633.6 \ g/mol) \\ Calcd \ C \ 32.23 \ H \ 5.09 \ N \ 4.42 \ S \ 10.12 \ \%, \\ Found \ C \ 33.07 \ H \ 5.05 \ N \ 3.94 \ S \ 10.20 \ \%. \end{array}$

4b was prepared from 0.8 mmol (1 ml of the DMSO stock solution) of **2a** and 0.34 g (0.5 mmol) of (Bu₃P)₂PtCl₂ in 10 ml of DMSO (reaction time: 22 h, the colour changes from dark red-brownish to red) and the purification (column chromatography: hexane/ethyl acetate 5:1) of the product was carried out as described for **3**. Red-orange powder. – Yield 0.28 g (55 %), m. p. > 250 °C (dec.). – IR (KBr): $\nu = 3184$ cm⁻¹ (w, br), 3086 (w), 3050 (w) (OH/NH), 1712 (s), 1679 (m), 1632 (s) (C=O), 1463 (m, br), 1396 (vs, br) (C=C/C=O). – ¹H NMR (CDCl₃): $\delta = 7.32$ (br. s, 2H, NH). – ³¹P NMR (CHCl₃): $\delta = -2.92$ (s, ¹J(¹⁹⁵Pt-³¹P) = 2860 Hz)

 $C_{29}H_{56}N_2O_3P_2PtS_2 (M = 801.9 \text{ g/mol})$

Calcd C 43.44 H 7.04 N 3.49 S 8.00 %, Found C 42.10 H 6.92 N 3.23 S 9.38 %.

4c was prepared from 0.4 mmol (0.5 ml of the DMSO stock solution) of **2a** and 0.12 g (0.3 mmol) of (dppe)PtCl₂ in 10 ml of DMSO (reaction time: 20 h, colour: yellow suspension). The product was purified as described for **3**. Yellow powder. – Yield 0.32 g (81 %), m. p. > 250 °C (dec.). – IR (KBr): ν = 3291 cm⁻¹ (w, br), 3191 (w), 3074 (w, br) (OH/NH), 1748 (m), 1724 (s), 1677 (s), 1625 (s) (C=O), 1435 (s), 1406 (vs, br) (C=C/C=O). – ¹H NMR (CDCl₃): δ = 2.35 - 2.48 (m, 4H, PCH₂CH₂P). – ³¹P NMR (CDCl₃): δ = 40.48 (s, ¹*J*(¹⁹⁵Pt-³¹P) = 2877 Hz).

 $\begin{array}{l} C_{31}H_{26}N_2O_3P_2PtS_2 \ (M=795.7 \ g/mol)\\ Calcd \ C \ 46.79 \ H \ 3.29 \ N \ 3.52 \ S \ 8.06 \ \%,\\ Found \ C \ 45.96 \ H \ 3.29 \ N \ 3.18 \ S \ 8.33 \ \%. \end{array}$

4d was prepared from 0.4 mmol (0.5 ml of the DMSO stock solution) of **2a** and 0.23 g (0.3 mmol) of [(-)-DIOP]PtCl₂ in 10 ml of DMSO (reaction time: 2 d, colour changes from orange to bright yellow). The product was purified as described for **3**. Yellow powder. – Yield 0.26 g (59 %), m. p. > 250 °C (dec.). – IR (KBr): ν = 3429 cm⁻¹ (m, br), 3208 (w), 3071 (w, br) (OH/NH), 1721 (s), 1681 (s), 1651 (s) (C=O), 1434 (s), 1418 (vs, br) (C=C/C=O). – ¹H NMR (CD₂Cl₂): δ = 1.25 (s, 6H, CH₃), 2.64 / 3.27 (m, 6H, CH₂), 4.02 (m, 2H, OCH). – ³¹P NMR (CD₂Cl₂): δ = 2.25 (s, ¹*J*(¹⁹⁵Pt-³¹P) = 2853 Hz)

 $\begin{array}{l} C_{36}H_{34}N_2O_5P_2PtS_2 \ (M=895.8 \ g/mol)\\ Calcd \ C \ 48.27 \ H \ 3.83 \ N \ 3.13 \ \%,\\ Found \ C \ 47.26 \ H \ 4.11 \ N \ 2.87 \ \%. \end{array}$

5a was prepared from 0.8 mmol (1 ml of the DMSO stock solution) of **2b** and 0.34 g (0.5 mmol) of (Bu₃P)₂PtCl₂ in 10 ml of DMSO (reaction time: 22 h, colour: bright-yellow). The product was purified as described for **3**. Yellow powder. – Yield 0.25 g (60 %), m. p. > 250 °C (dec.). – IR (KBr): ν = 3435 cm⁻¹ (w), 3202 (m), 3065 (m) (OH/NH), 1703 (s), 1670 (s), 1645 (s) (C=O), 1462 (s), 1395 (vs, br) (C=C/C=O). – ¹H NMR (CD₃CN): δ = 8.28 (s, 1H, NH), 3.09 (s, 3H, NCH₃). – ¹³C NMR (CD₂Cl₂): δ = 26.47 (s, NCH₃), 108.35 (t, ³*J*(¹⁹⁵Pt-¹³C) = 37 Hz, ⁴*J*(³¹P-¹³C) = 2 Hz, S₂C=C), 151.07, 160.89, 162.00 (s, C=O), 216.50 (s, ²*J*(¹⁹⁵Pt-¹³C) = 79 Hz, S₂C =C). – ³¹P NMR (CD₃CN): δ = -3.03 / –3.07 (AB spin systeme, ¹*J*(¹⁹⁵Pt-³¹P) = 2844 / 2847 Hz, ²*J*(³¹P-³¹P) = 4.0 Hz).

 $\begin{array}{l} C_{30}H_{58}N_2O_3P_2PtS_2 \ (M=816.0 \ g/mol)\\ Calcd \ C \ 44.16 \ H \ 7.16 \ N \ 3.43 \ \%,\\ Found \ C \ 44.22 \ H \ 7.19 \ N \ 3.34 \ \%. \end{array}$

5b was prepared from 0.8 mmol (1 ml of the DMSO stock solution) of **2c** and 0.34 g (0.5 mmol) of $(Bu_3P)_2PtCl_2$ in 10 ml of DMSO (reaction time: 2 d, the

colour changes from red to yellow) and the product was purified as described for **3** (column chromatography: hexane / ether 5:1). Yellow powder, – Yield 0.16 g (36 %), m. p. 171 °C. – IR (KBr): $\nu = 3429 \text{ cm}^{-1}$ (w), 3238 (w, br), 3063 (w) (OH/NH), 1711 (vs), 1675 (s), 1640 (s) (C=O), 1434 (s), 1401 (vs, br) (C=C/C=O). – ¹H NMR (CDCl₃): $\delta = 7.36$ (s, 1H, NH), 3.09 (m, 2H, NCH₂). – ³¹P NMR (CDCl₃): $\delta = -2.65 / -2.86$ (AB spin system, ¹*J*(¹⁹⁵Pt-³¹P) = 2855 / 2858 Hz, ²*J*(³¹P-³¹P) = 21.5 Hz).

 $\begin{array}{l} C_{35}H_{68}N_2O_3P_2PtS_2 \ (M=886.1 \ g/mol)\\ Calcd \ C \ 47.44 \ H \ 7.74 \ N \ 3.16 \ S \ 7.24 \ \%,\\ Found \ C \ 47.50 \ H \ 7.53 \ N \ 3.00 \ S \ 7.25 \ \%. \end{array}$

5c was prepared from 0.8 mmol (1 ml of the DMSO stock solution) of **2d** and 0.34 g (0.5 mmol) of (Bu₃P)₂PtCl₂ in 10 ml of DMSO (reaction time: 22 h, colour: orange-yellow). The purification (column chromatography: hexane / ethyl acetate 2:1) of the product was carried out as described for **3**. Yellow powder. – Yield 0.21 g (44 %), m. p. 129 °C. – IR (KBr): ν = 3338 cm⁻¹ (w), 3163 (w), 3117 (w) (OH/NH), 1716 (s), 1662 (s), 1633 (s) (C=O), 1450 (s), 1406 (vs, br) (C=C/C=O). – ¹H NMR (CDCl₃): δ = 7.38 (s, 1H, NH), 3.83 (m, 2H, NCH₂). – ¹³C NMR (CDCl₃): δ = 40.42 (s, NCH₃), 108.85 (s, S₂C=C), 150.63, 160.92, 162.51 (s, C=O), 217.54 (s, S₂C =C). – ³¹P NMR (CDCl₃): δ = -2.75 / -3.12 (AB spin system, ¹*J*(¹⁹⁵Pt-³¹P) = 2857 / 2859 Hz, ²*J*(³¹P-³¹P) = 21.4 Hz).

 $C_{41}H_{80}N_2O_3P_2PtS_2$ (M = 970.2 g/mol)

Calcd C 50.76 H 8.31 N 2.89 S 6.61 %, Found C 50.86 H 8.16 N 2.93 S 6.71 %.

5d: A mixture of **2c** (0.8 mmol, 1 ml of the DMSO stock solution) and of (Ph₃P)₂PtCl₂ (0.40 g, 0.5 mmol) in 10 ml of DMSO was stirred for 2 d. During this time the colour of the solution changed from orange to red. After addition of 10 ml of water the suspension was extracted with three 20-ml portions of dichloromethane. The combined organic extracts were washed with 20 ml of water and dried with sodium sulfate. The solvent was removed in vacuo to leave a yellow powder. – Yield 0.28 g (55 %), m. p. (dec.) > 250 °C. – IR (KBr): ν = 3421 cm⁻¹ (m, br), 3238 (w, br), 3063 (w) (OH/NH), 1711 (vs), 1675 (s), 1640 (s) (C=O), 1434 (s), 1417 (vs, br) (C=C/C=O). – ¹H NMR (CDCl₃): δ = 9.53 (s, 1H, NH), 2.95 (m, 2H, NCH₂). – ³¹P NMR (CDCl₃): δ = 17.93 / 18.60 (AB spin system, ¹*J*(¹⁹⁵Pt-³¹P) = 2989 / 2885 Hz, ²*J*(³¹P-³¹P) = 23.2 Hz).

 $\begin{array}{l} C_{47}H_{44}N_2O_3P_2PtS_2 \ (M=1006.0 \ g/mol)\\ Calcd \ C \ 56.11 \ H \ 4.41 \ N \ 2.78 \ \%,\\ Found \ C \ 55.85 \ H \ 4.90 \ N \ 3.06 \ \%. \end{array}$

6a was prepared from 0.8 mmol (1 ml of the DMSO stock solution) of **2e** and 0.34 g (0.5 mmol) of $(Bu_3P)_2PtCl_2$ in 10 ml of DMSO (reaction time: 2 d,

	4a	4c	5a	8
Formula	$C_{17}H_{32}N_2O_3P_2PtS_2$	$C_{39}H_{50}N_2O_7P_2PtS_6$	$C_{30}H_{58}N_2O_3P_2PtS_2$	$C_{22}H_{39}N_5O_3P_2PtS_2$
$M_{\rm r}$	633.6	1108.2	815.9	742.7
Crystal size [mm]	$0.32 \times 0.3 \times 0.22$	$0.1 \times 0.15 \times 0.2$	0.6 imes 0.5 imes 0.5	$0.2 \times 0.3 \times 0.4$
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	<i>P</i> 2 ₁ /c	<i>P</i> 2 ₁ /c	$P2_1/n$
a [Å]	10.189(2)	14.345(2)	10.412(2)	14.441(3)
<i>b</i> [Å]	17.035(5)	14.920(2)	21.879(16)	13.446(2)
<i>c</i> [Å]	14.285(3)	20.643(3)	16.834(7)	18.281(3)
β [°]	103.88(2)	90.973(6)	99.19(1)	107.08(1)
$V[Å^3]$	2407(1)	4417(1)	3786(3)	3393(1)
$\rho_{\text{calcd}} [\text{g cm}^{-3}]$	1.748	1.666	1.432	1.509
Ζ	4	4	4	4
<i>F</i> (000) [e]	1248	2232	1664	1536
<i>T</i> [K]	213(2)	193(2)	223(2)	293(2)
hkl Range	$0,+12/-20,0/\pm 16$	$\pm 18/\pm 18/\pm 26$	$-12,0/0,+26/\pm19$	0,+16/0,+16/±22
2Θ Range [°]	3.78 - 50.00	2.84 - 58.38	3.08 - 50.00	3.82 - 53.16
Measured refl.	4476	25042	6957	6606
Unique refl.	4224	8939	6578	5982
Observed refl.	$3204 [F > 4\sigma F]$	6426 $[F > 4\sigma F]$	4833 $[F > 4\sigma F]$	2438 $[F > 4\sigma F]$
Min./max. transm.	0.132/0.215	0.352/0.460	0.077/0.128	0.343/0.723
Refined parameters	242	522	361	368
$RI[F >4\sigma F]$	0.0420	0.0243	0.0539	0.0877
wR2	0.1164	0.0495	0.1420	0.2105
$\rho_{\rm fin}({\rm max/min})[{\rm e}{\rm \AA}^{-3}]$	1.171/-0.772	0.747/-0.567	1.597/-2.395	1.229/-1.590
Goodness-of-fit	1.056	1.147	1.060	1.144

Table I. Crystal data and refinement details for complexes 4a, 4c, 5a and 8.

colour changes from red to yellow). The product was purified as described for **3**. Yellow powder. – Yield 0.20 g (49 %), m. p. 180 °C. – IR (KBr): $\nu = 1701 \text{ cm}^{-1}$ (vs), 1648 (s), 1640 (s) (C=O), 1454 (s), 1394 (vs, br) (C=C/C=O). – ¹H NMR (CD₂Cl₂): $\delta = 3.21$ (s, 6H, NCH₃). – ³¹P NMR (CH₂Cl₂): $\delta = -3.93$ (s, ¹*J*(¹⁹⁵Pt-³¹P) = 2845 Hz).

 $C_{31}H_{60}N_2O_3P_2PtS_2$ (M = 830.0 g/mol)

Calcd C 44.86 H 7.29 N 3.37 %,

Found C 46.00 H 7.42 N 3.25 %.

6b: A mixture 0.8 mmol (1 ml of the DMSO stock solution) of **2e** and 0.40 g (0.5 mmol) of (Ph₃P)₂PtCl₂ in 10 ml of DMSO was stirred for 20 h. During this time the colour of the solution changed from orange to dark red. After addition of 10 ml of water the suspension was extracted with three 20-ml portions of dichloromethane. The combined organic extracts were washed with 20 ml of water and dried with sodium sulfate. The solvent was removed in vacuo to leave a yellow powder. – Yield 0.26 g (54 %), m. p. (dec) > 250 °C. – IR (KBr): ν = 1708 cm⁻¹ (m), 1648 (s) (C=O), 1448 (s), 1419 (vs, br) (C=C/C=O). – ¹H NMR (CDCl₃): δ = 3.19 (s, 6H, NCH₃). – ³¹P NMR (CDCl₃): δ = 18.59 (s, ¹*J*(¹⁹⁵Pt-³¹P) = 2979 Hz).

C₄₃H₃₆N₂O₃P₂PtS₂ (949.9); CHN analysis not satisfying.

6c was prepared from 0.8 mmol (1 ml of the DMSO stock solution) of **2e** and 0.34 g (0.5 mmol) of (Bu₃P)₂PtCl₂ in 10 ml of DMSO (reaction time: 22 h, colour changes from red to orange). The product was purified as described for **3**. Yellow powder. – Yield 0.28 g (57 %), m. p. 191 °C. – IR (KBr): $\nu = 1702 \text{ cm}^{-1}$ (s), 1649 (vs) (C=O), 1445 (s), 1399 (vs, br) (C=C/C=O). – ¹H NMR (CD₂Cl₂): $\delta = 5.21$ (s, 4H, NCH₂). – ¹³C NMR (CD₂Cl₂): $\delta = 44.18$ (s, NCH₂), 152.32, 161.53, (s, C=O), 217.78 (s, S₂C =C). – ³¹P NMR (CD₂Cl₂): $\delta = -3.23$ (s, ¹*J*(¹⁹⁵Pt-³¹P) = 2847 Hz).

 $C_{43}H_{68}N_2O_3P_2PtS_2$ (M = 982.3 g/mol)

Calcd C 52.58 H 6.98 N 2.85 S 6.53 %, Found C 52.18 H 6.72 N 2.96 S 7.00 %.

7: A mixture 0.8 mmol (1 ml of the DMSO stock solution) of **2c** and 0.24 g (0.5 mmol) of (2,9-dimethylphenanthroline)PtCl₂ in 10 ml of DMSO was stirred for 22 h. During this time the colour of the suspension changed from dark brown to orange. After addition of 10 ml of water the suspension was extracted with three 20-ml portions of dichloromethane. The combined organic extracts were washed with 20 ml of water and dried with sodium sulfate. The solvent was removed in vacuo to leave a yellow powder which was washed with 30 ml of hexane. Orange powder. – Yield 0.18 g (53 %), dec. > 220 °C. – IR (KBr): ν = 3424 cm⁻¹ (w, br), 3175 (w, br), 3030 (w, br), 1710 (s), 1659 (s), 1632 (vs) (C=O), 1410 (vs, br) (C=C/C=O). – ¹H NMR (CDCl₃): δ = 7.58 (s, 1H, NH), 3.88 (m, 2H, NCH₂), 3.08 / 3.09 (s, 6H, CH₃).

 $C_{25}H_{26}N_4O_3PtS_2$ (M = 689.7 g/mol)

Calcd C 43.54 H 3.80 N 8.12 %,

Found C 41.61 H 3.93 N 7.51 %.

8: Complex 4a (0.063 g, 0.1 mmol) was dissolved in 5 ml of dichloromethane and added to a solution of 2,6-diaminopyridine (0.012 g, 0.1 mmol) in 1 ml of DMSO to give single co-crystals of 8 within 8 d. Yellow plates.

Crystal structure determinations of 4a, c, 5a, and 8 [24]

A single crystal of **4a**, **5a** and **8**, respectively, was mounted in a glass capillary. After optical alignment 20-25 reflections were autocentered, and the dimensions of the unit cell determined on a Siemens P4 instrument operating with graphite monochromatized Mo-K_{α} radiation. Data collection was performed in the $\omega/2\theta$ mode with variable scan speed. The data were then reduced by applying Lorentz and polarisation correction as well as empirical absorption correction based on ψ -scans. A single crystal of compound **4c** was mounted on a glass fiber

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with perfluoroether oil and transferred to a Siemens P4 diffractometer equipped with a CCD area detector. The dimensions of the unit cell were derived from the reflections with $I > 10 \sigma(I)$ on four sets of 15 frames ($\Delta \phi = 0.3^{\circ}$). Data were collected with an exposure time of 10 s per frame, and 1296 frames were collected at two different χ settings with $\Delta \phi = 0.3^{\circ}$ between the next frame. Data were reduced with the program SAINT, and absorption correction was performed using all data with $I > 10 \sigma(I)$ in a semiempirical procedure.

The structures were solved by Direct Methods using the program SHELXL 1993. Anisotropic thermal parameters were applied in the refinement of nonhydrogen atoms. Hydrogen atoms were placed in calculated positions and included in the refinement by applying a riding model. However, hydrogen atoms of NH groups were taken from difference Fourier peaks, and were freely refined with fixed isotropic U_i . Selected data of the experimental procedures are summarised in Table I.

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