An Acyclic Diaminocarbene Complex of Platinum Formed by Desulfurization of 1,3-Bis(3-methylpyridin-2-yl)thiourea

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The reaction of the ambidentate ligand 1,3-bis(3-methylpyridin-2-yl)thiourea (**1**) with $[PtCl_2(dmso)_2]$ in dichloromethane led to formation of a poorly soluble compound **2**, characterized as a conventional chelate complex $[PtCl_2(\mathbf{1})] = \mathbf{2}$. Reaction in methanol resulted in desulfurization to produce a fluorescing cationic diaminocarbene–platinum(II) complex **3**, the structure of which was elucidated by X-ray crystallography, mass spectrometry and NMR. Experimental findings were supported by DFT calculations.

Introduction

Acyclic diamino carbenes (ADC) and their metal complexes have attracted great interest in recent years due to their similarities with N-heterocyclic carbenes (NHC). Compared to NHCs which are widely used as components of catalysts, ADCs generally have a stronger σ donor character and a wider N–C–N angle, allowing for a closer approach of a coordinated metal center to provide better steric control.[1,2]

Catalytic applications of palladium- and platinum–ADCs in intermolecular Heck,[3–5] Buchwald-Hartwig, Sonogashira and Suzuki-Miyaura cross-coupling and several intramolecular cyclization reactions[1,6–12] as well as hydrosilylation have been published, although not as widely as the corresponding palladium NHC systems which have found very broad application as catalysts for such coupling reactions.[1,13–19]

Generation of ADC metal complexes may be accomplished by direct complexation of the free carbenes or by metal-mediated nucleophilic addition to isonitriles.[1,4,6–8,20–32] Recently, a new route was reported using aminonitrones with $[PtCl_2(dmso)_2]$ as the starting materials.[33]

Using direct complexation of carbenes by a metal, the free ADC must be generated in an initial step.

There are examples in the literature[34] where the C=S group of a thiourea compound was converted to C–Cl in a desulfurization reaction by the use of oxalyl chloride. Reaction of Pd^{II} precursors with the thus generated ADC yielded the corresponding palladium complexes.[34]

Apart from synthesizing ADC metal complexes, desulfurization reactions of thiourea compounds have been a subject of ongoing interest because the resulting carbodiimides are used as dehydrating agents in organic syntheses.[35,36] For desulfurization reactions quite toxic reagents are usually required.[37,38] It has been shown that the desulfurization of N,N-dimethylthioformamide by hydrosilane R_3SiH takes place in the presence of an iron complex. The suggested mechanism of C=S cleavage involves an iron carbene complex which was characterized by X-ray spectroscopy.[39,40]

Thiourea compounds are highly versatile organosulfur materials with diverse uses ranging from pharmacological applications, including anion transport in biological systems,[41–44] to organocatalysis of important reactions such as Diels-Alder cycloadditions and Friedel-Crafts alkylations, mainly due to their capacity for multiple hydrogen bonding.[44] In addition, the coordination chemistry of thiourea and of its substituted derivatives has attracted attention owing to the availability of different coordination sites in these molecules, coupled with diverse biological activities.[45–46] In addition, thiourea compounds are used as supporting agents in combination with cisplatin during tumor therapy to inhibit the coordination of Pt^{II} to sulfur containing enzymes and thus to reduce the toxic side effects of cisplatin.[47–49] Recently Pt^{II} complexes of NHCs where platinum is additionally coordinated to a pyridine ring were found to be effective in tumor therapy.[50]

There are several examples for reactions of Pt^{II} complexes with thiourea itself and substituted thiourea ligands such as 2,2′-dipyridyl-thiourea where nitrogen and sulfur can serve as coordination sites for Pt^{II}.[45,46,51–59]

During ongoing studies in our lab, the reaction of 1,3-bis(3-methylpyridin-2-yl)thiourea **1** with $[PtCl_2(dmso)_2]$ in dichloromethane (Scheme 1) was found to give a very insoluble non-fluorescing Pt complex **2** which could not easily be purified.

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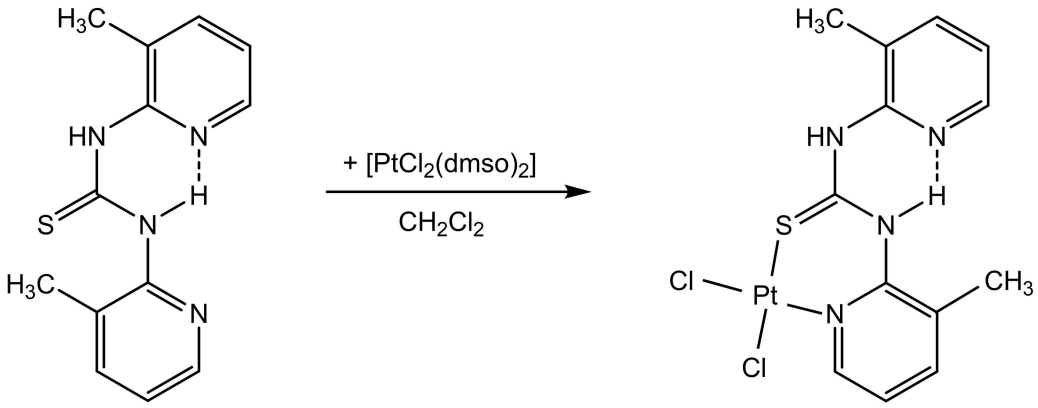


1 **2**

Scheme 1. Reaction of **1** with $[PtCl_2(dmso)_2]$ in CH_2Cl_2.

However, a single crystal of this complex was obtained by the slow evaporation of a hot acetonitrile solution. X-Ray analysis (cf. below) showed the expected[60] *N*,*S* coordinated platinum compound **2** where the metal atom is bound to the *S* of the thiocarbonyl group and to an *N* atom of one of the picoline rings in a chelating fashion (Scheme 1).

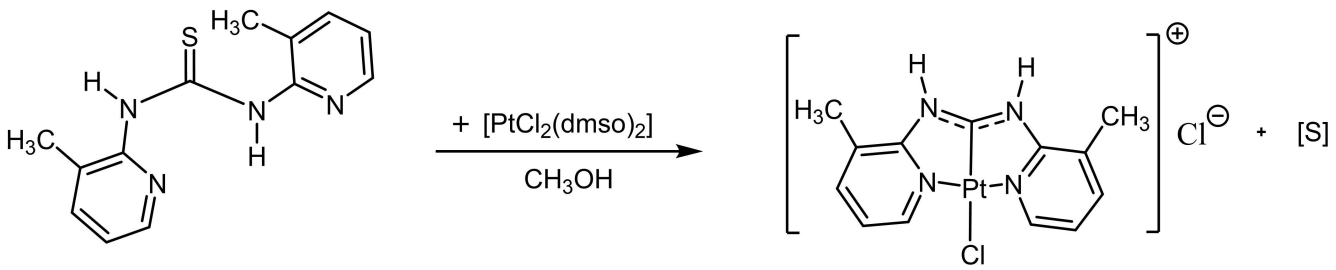
Along with this expected complex **2** there was a further product **3** which always formed during purification attemps. In this work we report the synthesis of this product **3** in a pure form by the reaction of the 1,3-bis(3-methylpyridin-2-yl)thiourea (**1**) with $[PtCl_2(dmso)_2]$ using methanol as the reaction solvent and a reaction time of 24 hours. The obtained product is characterized as an air-stable fluorescent ADC–Pt complex (**3**) which is formed via desulfurization (Scheme 2). This type of direct synthesis of an air stable Pt–ADC complex presents an alternative pathway to the above mentioned procedures. It is also a non-toxic way of S removal from a thiourea compound. The complex **3** is characterized by elemental analysis, ^{1}H- and ^{13}C-NMR, mass spectrometry and single crystal X-ray structural determination. The experimental results are supported by DFT calculations.

Results and Discussion

The synthesis of the ligand 1,3- bis(3-methylpyridin-2-yl) thiourea (**1**) was previously reported in the literature.[61] Its X-ray single crystal structure analysis[62] was reproduced here at 100 K and can be found under the CCDC registration number 1979822.

The X-ray crystal structure analysis could be performed for compound **2** because single crystals were obtained from hot acetonitrile. In the molecular structure, the platinum is coordinated to sulfur and to the nitrogen atom of one of the picoline rings, resulting in an asymmetrical, non-fluorescing complex with a six-membered chelate ring (Figure 1, Table S1, Table 1). From the X-ray investigation of the lattice it was seen that the intermolecular Pt–Pt distance is 810 pm, indicating no interaction of the platinum centers.

Hydrogen bonding between N4 and H1 N1 is observed in the structure of complex **2** with a corresponding N1–N4 distance of 258 pm. According to DFT this distance is calculated at 270.9 pm (Table 1). The calculations show that the picoline ring containing C8 as well as the N3, C1, N1, H1 and S1 atoms lie in the same plane. The second picoline ring which contains C2 lies in a plane together with N1 and Pt1. The angle between



1 **3**

Scheme 2. Reaction of **1** with $[PtCl_2(dmso)_2]$ in CH_3OH.

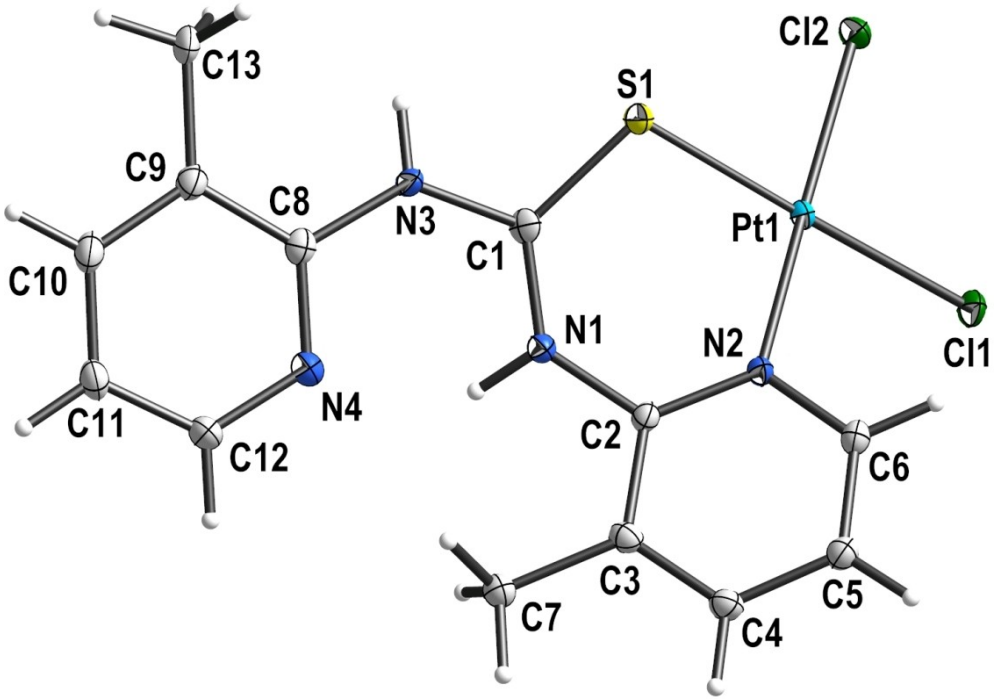


Figure 1. Molecular structure of the platinum complex **2** in the crystal.

Table 1. Experimental and calculated bond lengths (pm) and angles (°) for complex **2**.

bond lengths/pm	exp.	calc.
S1–C1	170.3(3)	169.8
N1–C2	139.5(3)	141.0
N1–C1	134.2(3)	134.9
N3–C8	140.4(3)	140.2
N3–C1	135.2(3)	137.5
C2–N2	135.4(3)	134.9
Pt1–N2	202.4(2)	207.9
Pt1–S1	223.65(7)	234.6
Pt1–Cl1	234.47(6)	237.6
Pt1–Cl2	230.26(7)	234.6
N1(H)–N4	258	270.9
bond angles/°		
C1–N1–C2	130.1(2)	129.4
C1–N3–C8	128.5(2)	131.9
Cl2–Pt1–Cl1	89.29(2)	91.0
S1–Pt1–C11	176.11(3)	175.9
S1–Pt1–C12	87.79(3)	87.7
N2–Pt1–C11	91.27(6)	90.6
N2–Pt1–C12	177.02(7)	177.8
N2–Pt1–S1	91.78(6)	90.8
C1–S1–Pt1	105.07(9)	100.4

these two planes, each containing a picoline ring, was DFT calculated at 22.74° while the experimental angle is 27.82°. Overall this is a more planar arrangement than that of the free ligand **1** with 64.16° dihedral angle in the crystal (experimental value). The six-membered chelate platinacycle is not planar, with an angle of 53.18° between the S–Pt–N2 and C1–N1–C2 planes from the X-ray structure (57.16° according to DFT calculations). Dihedral angles are given in Table S2.

Crystals of **3** suitable for X-ray analysis were obtained from the filtrate in methanol. Twinning impeded the structure determination of compound **3** significantly, because a low R(int) value faked a C-centred orthorhombic cell, for which the structure determination failed completely. The final analysis revealed a two-component twin of a monoclinic C-centred cell with a nearly equal distribution of both twin domains (0.511(2): 0.489(2)). Details of this structure determination are summarized in the Table S1. Although the R(int) value of 0.047 is indicating a C-centred orthorhombic system, it was not possible to solve the structure for this setting. A low R(int) value may also be caused by twinning of a monoclinic system, with a more or less equal distribution of both twin domains. Furthermore, a detailed analysis of the recorded data revealed a glide plane. For these reasons, the original cell was transformed into the standard setting of a monoclinic C-centred crystal system with a c-glide plane.

For this monoclinic cell the structure could successfully be solved in the space group C2/c with a disordered organic ligand. The atoms Pt1, Cl1, Cl2 and C1 are not affected by this disorder. As a result of this disorder, the organic ligand is slightly tilted by 16.9(3) degrees ("up-position") in comparison to the original orientation of the ligand ("down-position") illustrated in Figure 2 (and Figure S1). Because of intermolecular interactions this disorder is not randomly distributed. An (101)-layer contains only ligands with the "down-position" whereas the adjacent (202)-layer contains only tilted ligands in the "up-position" etc. (Figure 2 and S1). The final result is a 50% disorder of the organic ligand in the "up-" and "down"-positions.

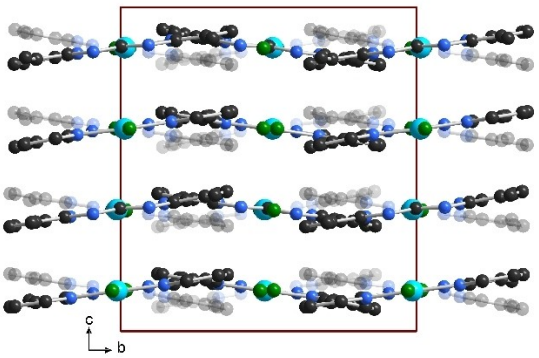


Figure 2. Lattice structure of complex **3** in the crystal (ball and stick model). Disordered atoms are visualized in transparent mode.

Table 2. Selected bond lengths (pm) and angles (°) for **3** (experimental and DFT calculated).

bonds	exp.	calc.
Pt1–C1	187.0(3)	190.0
Pt1–N2	201.0(9)	205.9
Pt1–N4	202.1(9)	205.9
Pt1–Cl1	235.87(8)	237.7
C1–N1	132.0(16)	134.6
C1–N3	136.4(13)	134.6
N1–C2	140.9(10)	141.6
N2–C6	134.7(9)	134.4
N2–C2	135.6(10)	135.7
N3–C8	139.2(10)	141.6
N4–C12	134.9(10)	134.4
N4–C8	136.5(10)	135.7
C2–C3	138.8(10)	139.4
C3–C4	139.8(11)	139.8
angles	**exp.**	**calc.**
C1–Pt1–N2	80.1(3)	80.6
C1–Pt1–N4	79.7(3)	80.6
C1–Pt1–Cl1	178.5(5)	180.0
N4–Pt1–Cl1	99.8(2)	99.4
N2–Pt1–Cl1	100.4(3)	99.4
N2–Pt1–N4	159.7(3)	161.2
N1–C1–N3	121.7(8)	125.9
N1–C1–Pt1	118.2(6)	117.0
N3–C1–Pt1	119.2(5)	117.0
C1–N1–C2	115.3(12)	116.0
C6–N2–C2	117.7(8)	119.9
C6–N2–Pt1	128.9(7)	128.0
C2–N2–Pt1	113.4(6)	112.1
C1–N3–C8	112.9(10)	116.0
C12–N4–C8	119.3(8)	119.9
C12–N4–Pt1	127.6(7)	128.0
C8–N4–Pt1	113.0(6)	112.1
N2–C2–C3	124.5(8)	123.1
N2–C2–N1	112.7(9)	114.3
C3–C2–N1	122.7(10)	122.6
C2–C3–C4	115.5(8)	116.0

The X-ray analysis (Table S1) revealed a symmetrical structure for a cation in **3**, where the largely planar configurated metal is chelated by the picoline nitrogen atoms (in *trans* position) and one carbene carbon, *trans* to a chloride ligand (Figure 3, Table 2). The uncoordinated chloride anion interacts with hydrogen atoms on N1 and N3 at N–Cl distances of 309.4 and 306.0 pm, respectively (weak hydrogen bonding, see Table S3). The sulfur atom from the ligand has been lost. While the fate of S (Scheme 2) could not be determined, the conversion of tetravalent carbon to carbene implies a redox process involving $S^{(-II)}/S^{(0)}$. The short Pt–C distance (187 pm) suggests the formation of an acyclic diaminocarbene (ADC) platinum complex. When compared to the Pt–C bond distances of N-heterocyclic carbene complexes which are generally in the range of 190–200 pm, this bond is relatively short.[63] This bond length is comparable to Pt–C of similar pincer type NHC Pt complexes found in the literature.[64] The structure shows a slightly distorted square planar arrangement typical for a Pt^{II} species. The Pt–N bonds are quite similar at 201.0 pm and 202.1 pm, respectively, and a relatively long Pt–Cl bond of 235.87 pm is situated *trans* to the short Pt–C bond. While the angles of about 120° at the carbene carbon reflect an sp^2 hybridization, the angles at the platinum(II) center are some-

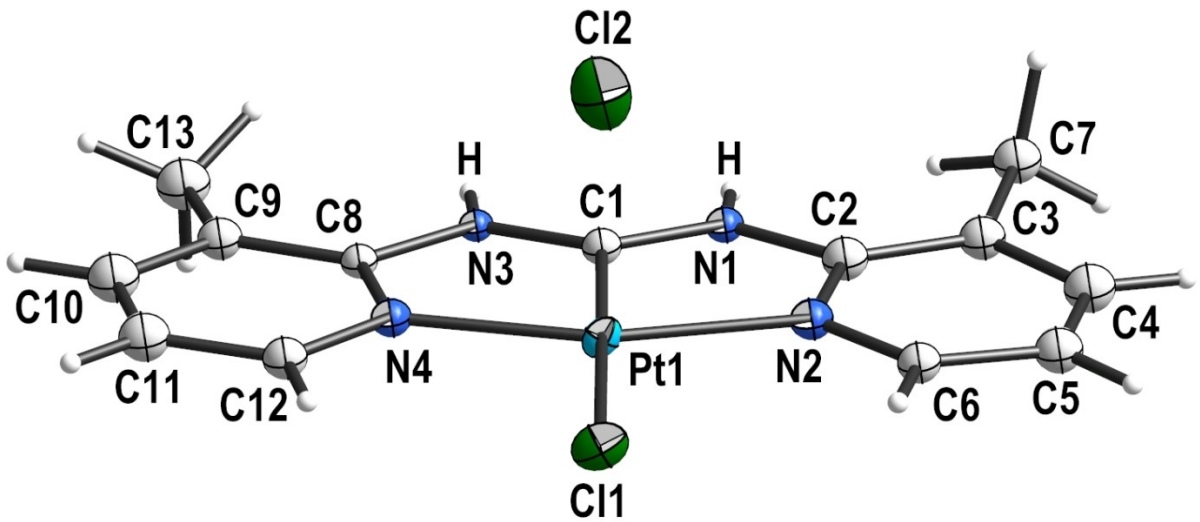


Figure 3. The molecular structure of **3** in the crystal.

what distorted from 90° due to the double chelate situation. The π interaction in the ligand unit is evident from the C1–N1 and C1–N3 bond lengths which are 132.0 and 136.4 pm, respectively. These values lie between C–N single bonds of about 147 pm and C=N double bonds of ca. 128 pm.[65–66] The N1–C1–N3 bond angle is 121.7°, indicative of a typical sp^2 hybridized carbene. The chlorine atom at the Pt atom in a *trans* position to the carbene forms an angle C1–Pt–Cl1 of 178.5°. One of the chloride ions on Pt in the starting complex $[PtCl_2(dmso)_2]$ now acts as an anion to the ADC–Pt complex cation.

The symmetrical structure is well supported by DFT calculations, displaying two *trans* Pt–N bonds surrounding Pt, a short Pt–C and a long Pt–Cl bond (Table 2). Table S4 gives the remaining experimental and calculated bond lengths and angles for complex **3.**

The crystal structure also reveals a short *intermolecular* Pt–Pt distance in the lattice at around 339 pm, indicating a Pt–Pt interaction.[64] The parallel arrangement of the Pt carbene planes (Figure 2) together with this short distance can be taken as favoring the strong fluorescence (Figure S7b).

In the ^{1}H-NMR spectrum of **3**, the signals of symmetrical picoline H nuclei at 8.63(d), 7.85 (d), and 7.26(t) in CD_2Cl_2 are shifted downfield with respect to those of the free ligand. The presence of only one signal for the picoline methyl groups at 2.57 ppm in dichloromethane and at 2.30 ppm in dmso is also a strong evidence for a symmetrical structure (Figure S2, (Figure S3). The presence of two N–H groups is apparent from peaks at 4.1 ppm in dmso-d_6 and at 3.6 ppm in CD_2Cl_2, respectively. In the ^{1}H-NMR spectra ^{195}Pt satellites of the picoline proton signals can be distinguished with Pt–H couplings of about 40 Hz (Figure 4).

Compared to the ^{13}C-NMR spectrum of the free ligand in dmso-d_6, the thiocarbonyl C signal at 179 ppm is replaced by a new downfield peak at 186.5 ppm that is assigned to the carbene carbon (Figure S4). ^{195}Pt–C (carbene) coupling could not be observed in the ^{13}C-NMR spectrum. The ^{13}C-NMR signals are again in accordance with a symmetrical product.

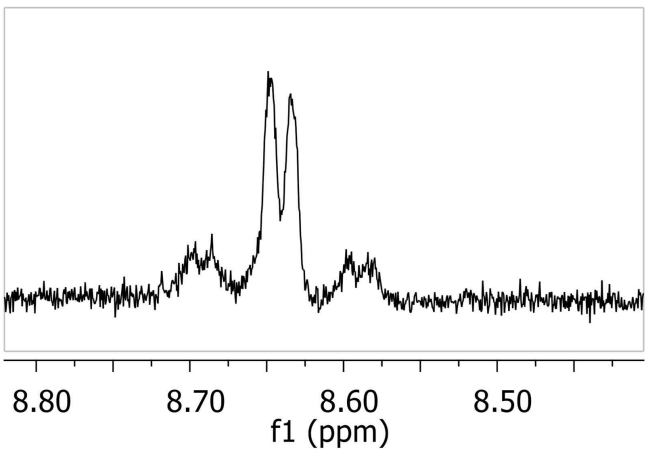


Figure 4. ^{195}Pt Satellites in the ^{1}H-NMR spectrum of **3** in CD_2Cl_2.

The IR spectrum of the pure ligand shows a band at 1157 cm^{-1} which can be attributed to the C=S stretching motion. In complex **3** this stretch is replaced by a newly formed band at 1610 cm^{-1} which can be attributed to a partial C=N double bond formation.

The mass spectrum of compound **3** has the molecular ion peak (M^+) at m/z = 457. The isotopic pattern is compatible with that simulated for $C_{13}H_{14}N_4PtCl^+$ (Figure S5a,b). The only extra peak in the mass spectrum at m/z = 912 can be attributed to (2 M^+-H^+) of **3** which is the dimerization product of **3**, confirmed by a simulated isotope pattern for $C_{26}H_{27}Cl_2N_8Pt_2^+$ (Figure S6a,b).

This type of dimerization or cluster formation of Pt compounds in the ESI-MS was previously reported in the literature.[67]

The UV-visible spectrum of **3** (Figure S7a) in acetonitrile gives a high intensity peak at 264 nm which is tentatively assigned to a π-π* intraligand transition. The smaller peaks at lower energy (at 345 and 430 nm) can be attributed to metal-to-ligand and ligand-to-metal charge transfer transitions. Fluorescence measurements of **3** in acetonitrile solution revealed emission peaks at 503 and 531 nm when irradiated by 345 nm light (Figure S7b).

In the solid state, complex **3** shows also strong emission. This is probably supported by the intermolecular Pt–Pt interaction occuring at a distance of 339 pm and by the parallel arrangement of the carbene planes in the lattice structure of the solid phase (Figure 2).

Conclusion

The reaction of $[PtCl_2(dmso)_2]$ with sterically constricted **1** proceeds to yield different products, depending on the solvent. Whereas a conventional N,S-chelated compound **2** of thiourea with *cis*-$PtCl_2$ is formed in aprotic dichloromethane, the conversion in methanol leads to a desulfurized material **3** with a tridentate (py)N–N(H)CN(H)–N(py) diaminocarbene ligand and one coordinated and one „free" chloride. While we refrain from mechanistic speculation it is tempting to associate the latter reaction in protic CH_3OH with hydrodesulfurization (HDS),[68] including C–S cleavage,[69] which are not uncommon processes involving platinum.

Experimental Section

Instrumentation

Elemental analyses were performed using a Perkin Elmer Analyzer 240. ESI und EI mass spectra were carried out with a Bruker Daltronics Microtof Q mass spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded using a Varian Gemini 400 MHz Spectrometer (Istanbul) and a Bruker AV250 instrument (resonance frequency 250.133 MHz, Stuttgart). In the proton spectra, the residual signal of the deuterated solvents was used as standard and referenced to TMS (δ = 0.00 ppm). The ^{13}C-NMR spectra were proton decoupled. UV-visible spectra were recorded with a Shimadzu UV 160 (range

200 nm to 2000 nm in quartz cuvets (Helma, thickness: 10 mm) or a Perkin Elmer Lambda 35 spectrometer. For IR spectra a Nicolet 6700 FT-IR spectrometer (Thermo Scientific) was used. Fluorescence spectra were run on a LS55 fluorescence spectrophotometer from Perkin Elmer. Cyclic voltammograms were recorded with the potentiostat M 273 A and the function generator M 175 (EG&G) using a three electrode arrangement (platinum working and counter electrode, silver pseudo reference electrode, internal standard ferrocene/ferrocenium (Fc^0/Fc^+)). The program used was Electrochemistry PowerSuite from Princeton Applied Research. All measurements were carried out under an argon atmosphere in a 0.1 M tetrabutylammonium hexafluorophosphate solution.

Syntheses

Ligand (1)

1,3-Bis(3-methylpyridin-2-yl)thiourea (**1**) was synthesized according to a general procedure.[61] NMR and MS data can be obtained from the supplementary material. X-Ray data can be found with the CCDC numbers 1475968 (120 K)[62] and CCDC 1979822 (100 K) (this work).

Complex 2

To a dichloromethane solution of **1** (0.034 g, 0.13 mmol) at 35 °C an amount of 0.0527 g (0.124 mmol) of $[PtCl_2(dmso)_2]$ in 5 ml CH_2Cl_2 was added and stirred for 4 hours under argon. The poorly soluble brown product was filtered and washed with dichloromethane. A hot acetonitrile solution of **2** gave yellow crystals suitable for single crystal determination upon solvent evaporization. Yield: 0.025 g (39%). Analysis for $C_{13}H_{14}Cl_2N_4PtS$ (524.33 g/mol): Calc. (found) % C 29.78 (29.45), H 2.69 (3.13), N 10.69 (9.60). **2** proved insufficiently soluble for NMR. MS(ESI): (calc for M^+-H-2Cl) m:z = 451.05(84), 452.057(100), 453.059(84); (found) 451.05(86), 452.05 (100), 453.05(88).

Complex 3

To a methanol solution of **1** (0.033 g, 0.13 mmol) an amount of 0.0527 g (0.124 mmol) of $[PtCl_2(dmso)_2]$ was added and stirred at 35 °C for 24 hours. The orange-colored fluorescent solid **3** was isolated by filtration and washed with diethylether. Yield: 0.022 g (35%). Analysis for $C_{13}H_{14}Cl_2N_4Pt$ (492.27 g/mol): Calc (found) % C 31.72 (31.12), H 2.87 (2.90), N 11.38 (11.05). ^{1}H-NMR (dmso-d_6): δ(ppm) = 8.22 (d, ^{3}J–Pt–H 40 Hz, 2H), 7.72 (d, 2H), 7.1 (t, 2H), 4.1 (2H), 2.30 (s, 6H) (Figure S2).^{1}H-NMR (CD_2Cl_2): δ (ppm) = 8.63 (d, ^{3}JPt–H 40 Hz, 2H), 7.85 (d, 2H), 7.26 (dd, 2H), 2.57 (s, 6H), 3.7 (s, 2H) (Figure S3). ^{13}C-NMR (dmso-d_6): δ (ppm) = 18.72 (CH_3), 118.16, 123.51, 142.8, 145.7, 165, 186 (NCN carbene) (Figure S4). MS (ESI, Figure S5, (Figure S6): calc. for $C_{13}H_{14}N_4PtCl^+$ m/z = 457 (M^+) and 420 (M^+-HCl), 912 ($C_{26}H_{27}N_8Cl_2Pt_2^+$)(2 M^+-H^+), 934 (2 M^+-2H^+ + Na^+). UV-Vis (acetonitrile): λ (nm) 264, 338, 420, 443. Fluorescence (acetonitrile, excitation wavelength 345 nm): λ(nm) 503, 531 nm. IR: ν (cm^{-1}) 3023 cm^{-1} (N–H), 1610 cm^{-1} (C=N). Cyclic voltammetry: At room temperature in CH_3CN/0.1 M Bu_4NPF_6 there was no reversible behavior observed.

Reaction in CD_3OD

To elucidate the progress of the reaction with $[PtCl_2(dmso)_2]$ in methanol, the reaction was run in CD_3OD at 35 °C under Ar and followed by ^{1}H-NMR spectroscopy at certain time intervals. Within the first 15–20 minutes the methanol-insoluble platinum precursor became soluble upon reacting with thiourea. The peaks of the methanol-soluble ligand vanished within the first half hour of the reaction and peaks of a new methanol-soluble intermediate started to appear. That non-fluorescent intermediate was constantly forming during the first 4 hours of the reaction. The CD_3OD solution gave the same ^{1}H-NMR signals that were present when the previously obtained insoluble *N,S* coordinated product (**2**) was treated with methanol during purification attempts. After reaction for six hours the orange-colored fluorescent product **3** started to precipitate.

Crystallography

Crystals suitable for X-ray diffraction of the Pt complex **2** (yellow needles) were prepared by slow evaporation from a saturated solution in hot acetonitrile. X ray diffraction data were collected using a Bruker Kappa APEX II Duo diffractometer with a graphite monochromator at 100 K. The radiation source was a fine-focus sealed tube using MoKα radiation at λ = 71.073 pm. Data reduction was performed with SAINT and numerical absorption correction with SADABS.[70] The structure was solved by dual-space methods with SHELXT-2018.[71] All non-hydrogen atoms were refined anisotropically. Excluding H(1 N) and H(3 N) all hydrogen atoms were calculated on idealized positions. The water molecule O1, O1F is disordered on two positions with a ratio of 0.502(5):0.498(5). Water hydrogen atoms are only deduced from adjacent acceptor centers. The CCDC number for **2** is 1979823.

Crystals suitable for X-ray diffraction of **3** (orange platelets) were obtained from a methanol solution. The data were collected as above (Bruker Kappa APEX II Duo). Data reduction was performed with SAINT and numerical absorption correction with SADABS.[70] The structure was solved by dual-space methods with SHELXT-2018.[71] With the exception of the disordered organic ligand, non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms are calculated on idealized positions using the riding model. Structure figures were generated with DIAMOND-4.[72] The CCDC number for **3** is 1986829. Additional crystallographic information is given in Table 1 and in Table S1, Table S2.

DFT Calculations

Density functional (DFT) calculations were carried out using the program package Gaussian 09[73] in the gas phase at 298 K. The Pt-complex was modeled making use of the hybrid functional B3LYP with the triple-ζ-basis set 6–311 + G(d,p) for the light atoms and LANL2DZ for platinum atom. The calculated bond lengths and angles are given in Table 1, Table 2, Table S2 and Table S4.

Deposition Numbers 1979822 (for **1**–100 K), 1979823 (for **2**), and 1986829 (for **3**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Carbene complex · Crystal structure · Desulfurization · Platinum · Thiourea

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