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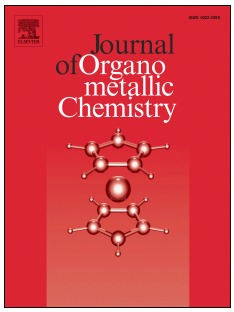

Synthesis, structure and catalytic activity of novel five-membered Pd(II) and Pt(II) metallaheterocycles based on 1,2-bis(3,5-dimethylisoxazol-4-yl-methylsulfanyl)ethane

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Synthesis, structure and catalytic activity of novel five-membered Pd(II) and Pt(II) metallaheterocycles based on 1,2-bis(3,5-dimethylisoxazol-4-yl-methylsulfanyl)ethane

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1. Introduction

To our knowledge, palladium and platinum N,O,S,Se-complexes containing heterocyclic ligands are efficient catalysts in modern organic synthesis. This is due to the new environmental protection policy that initiates the refusal to use traditional and easy oxidizable phosphorus-containing ligands [1].

Recently it has been reported [2] the unique behavior of isoxazoles as polydentate hybrid ligands used in the synthesis of organometallic catalysts. This is caused by the formation of so-called hemilabile complexes [3], in which one coordination group is easily displaced from the metal center, while the other one remains strongly bound to it [4]. This approach allows stabilizing palladium in different degrees of oxidation [5]. On the other hand, an important feature of nitrogen-containing ligands is the possibility of rotation around the C-N bond. This leads to a large steric flexibility of the ligand shape of the complex, which allows the catalyst to adjust to the conflicting steric requirements at different steps of the catalytic cycle [6].

Meanwhile, there are examples of palladated sulfur-carbon-sulfur (SCS) pincer complexes, which exhibit high catalytic activity in the Heck [7] and Suzuki reactions [8]. It was noted [9] that this effect is achieved due to the sulfur bivalence, namely, because of the larger cavity near the metal center in the SCS pincer complexes as compared to the PCP- or NCN-type complexes.

As a result, these complexes that act as catalysts can provide high product yield and stereoselectivity [10].

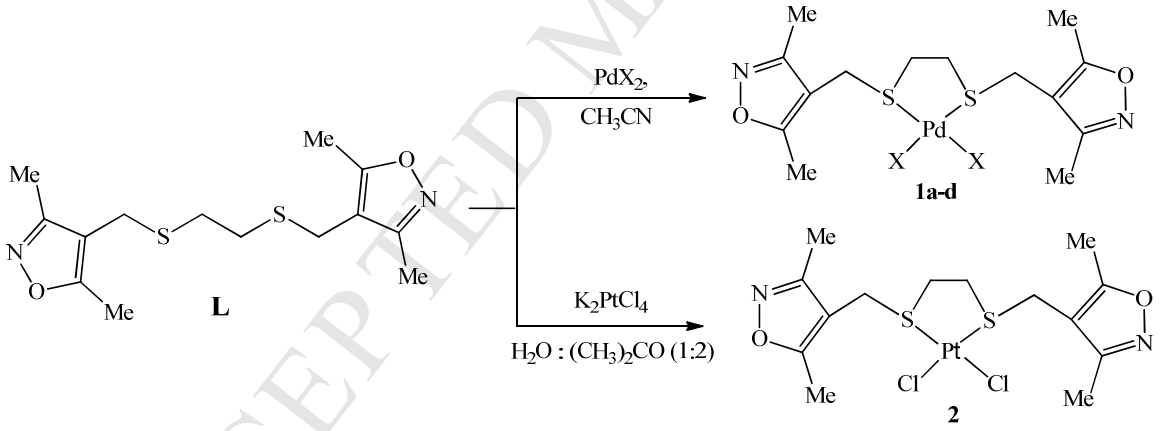
However, the investigations into the synthesis of metalla-sulfanyl-isoxazols and their catalytic properties have not been previously carried out although such ones would be effective for activation of the Pd-catalyzed reactions.

2. Results and discussion

Synthesis of five-member Pd(II) and Pt(II) metallaheterocycles

We have reported the synthesis of 1,2-bis(3,5-dimethylisoxazol-4-yl-methylsulfanyl)ethane [11] having different heteroatoms in a molecule: the nitrogen and oxygen atoms in isoxazole rings and the sulfur atoms in the aliphatic chain. Herein, this compound is presented as a promising polidentate ligand **L** forming cyclic palladium and platinum thiolate scaffolds.

The smooth synthesis of S,S-palladium(II**) 1a-d** and platinum(II) **2** metallaheterocycles (57-88% yield) was carried out by the reaction of ligand **L** with metal salts (1:1 molar ratio) at r. t. in acetonitrile, when using palladium salts [PdX_2, X = Cl, Br, CH_3COO, NO_2], or in aqueous acetone for K_2PtCl_4 (Scheme 1).



X = Cl (**1a**); Br (**1b**); CH_3COO (**1c**); NO_2 (**1d**)

Scheme 1. Synthesis of Pd(II) **1a-d** and Pt(II) **2** metallaheterocycles.

The resulting palladium and platinum novel five-membered metallaheterocycles were found to dissolve in DMSO and DMF, and cyclic palladium acetate complex **1c** is water-soluble.

The structures of **1a-d** and **2** were determined by means of ^{1}H, ^{13}C, and ^{15}N NMR spectroscopy, ESI (for **1a-d**), and MALDI TOF/TOF (for **2**) mass spectrometry.

The ^{1}H NMR spectrum of metallacycle **1a**, unlike that of precursor **L**, exhibits signals for protons of the methylene groups at sulfur as two sets of doublets (Fig. 1). This happens because

the two protons of each methylene group in the SCH_2CH_2S chain and SCH_2Iz fragment are diastereotopic [12]. Obviously, metallaheterocycle **1a** is a mixture of *anti*- and *syn*-isomers [13].

The temperature increase from 298 to 373 K resulted in a higher inversion rate of isomers and gave rise to exchange processes, which are manifested as signal broadening and coalescence of signals of the exchanging protons (Fig. 1).

Thus, when the temperature increases up to 373 K, the proton signals in each SCH_2Iz and SCH_2CH_2S fragments of metallaheterocycle compound **1a** become equivalent because of a merge to form broadened singlets. This process is reversible as evidenced by the averaging of the signals of both systems with heating from 293 K to 373 K and the subsequent formation of doublet-doublet signals upon cooling to 293 K.

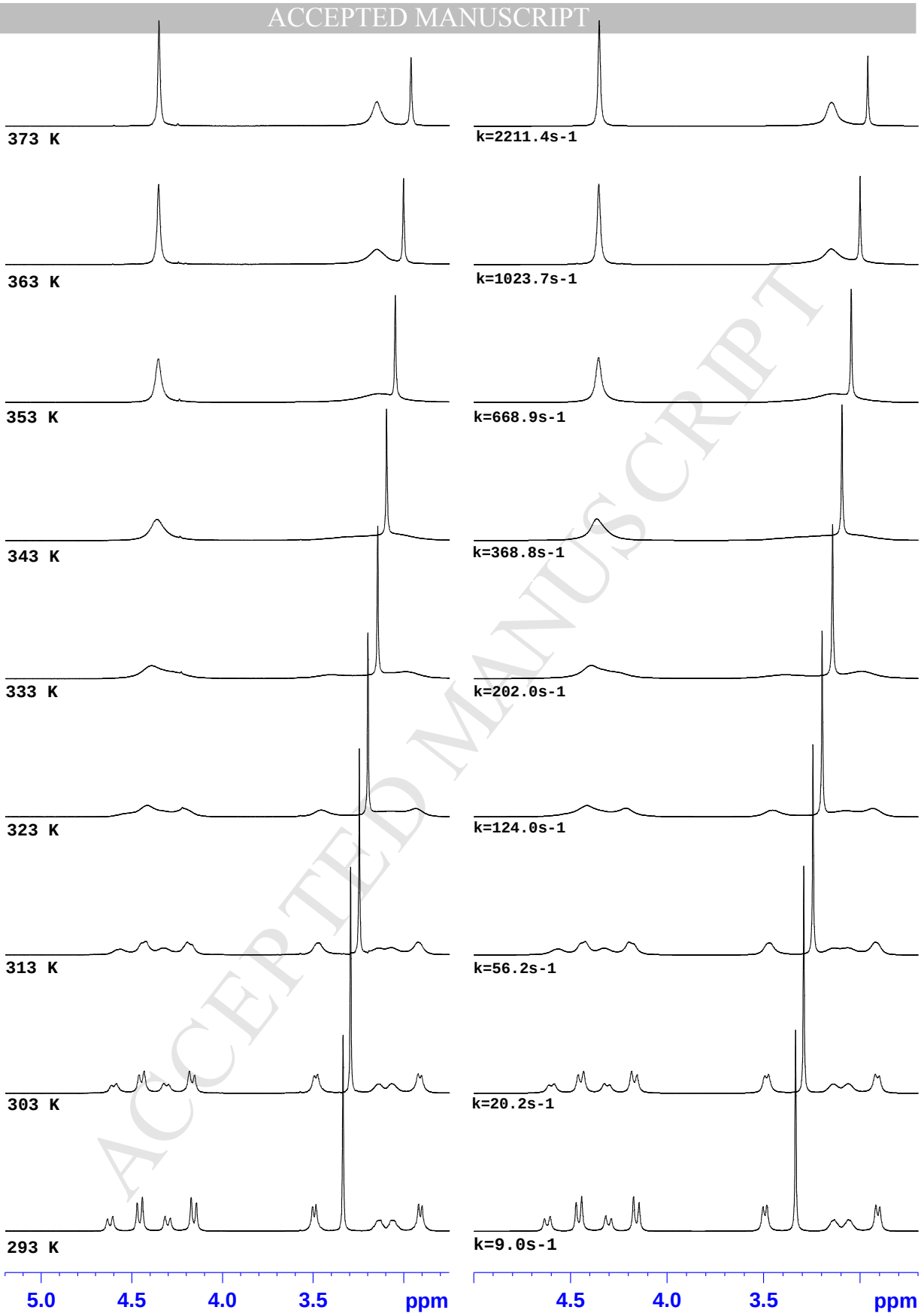


Fig. 1. Left: selected regions of the variable-temperature ^{1}H NMR spectra of Pd(II) **1a** complex in DMSO-d_6, 500 MHz. Right: simulated proton signals of the SCH_2Iz and SCH_2CH_2S fragments in cyclometallic compound **1a.**

The transition barrier for isomerization was determined at the coalescence temperature according to the Eyring equation**.**

We have performed the full-line-shape analysis of IzCH_2S and SCH_2CH_2S resonances in the variable-temperature ^{1}H NMR spectra (Fig. 2) [14]. The rate constants for the conversion between *anti*-**1a** and *syn*-**1a** were found to be 9.0 s^{-1} (293 K), 20.2 s^{-1} (303 K), 56.2 s^{-1} (313 K), 124.0 s^{-1} (323 K), 202.0 s^{-1} (333 K), 368.8 s^{-1} (343 K), 668.9 s^{-1} (353 K), 1023.7.2 s^{-1} (363 K), 2211.4 s^{-1} (373K). The activation enthalpy $\Delta H^{\neq}$ and activation entropy $\Delta S^{\neq}$, obtained from the Eyring plot, are 13.88 ± 0.6 kcal mol^{-1} and 4.9 ± 1.6 cal mol^{-1} K^{-1}, respectively. The free energies of activation at 298 K $\Delta G^{\neq}_{298}$ are 12.4 ± 0.6 kcal mol^{-1}.

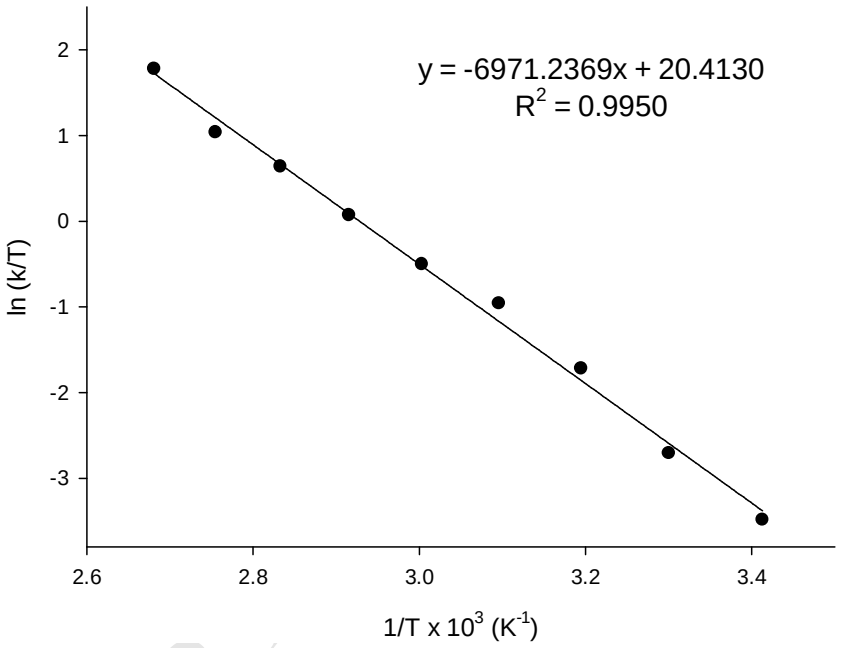
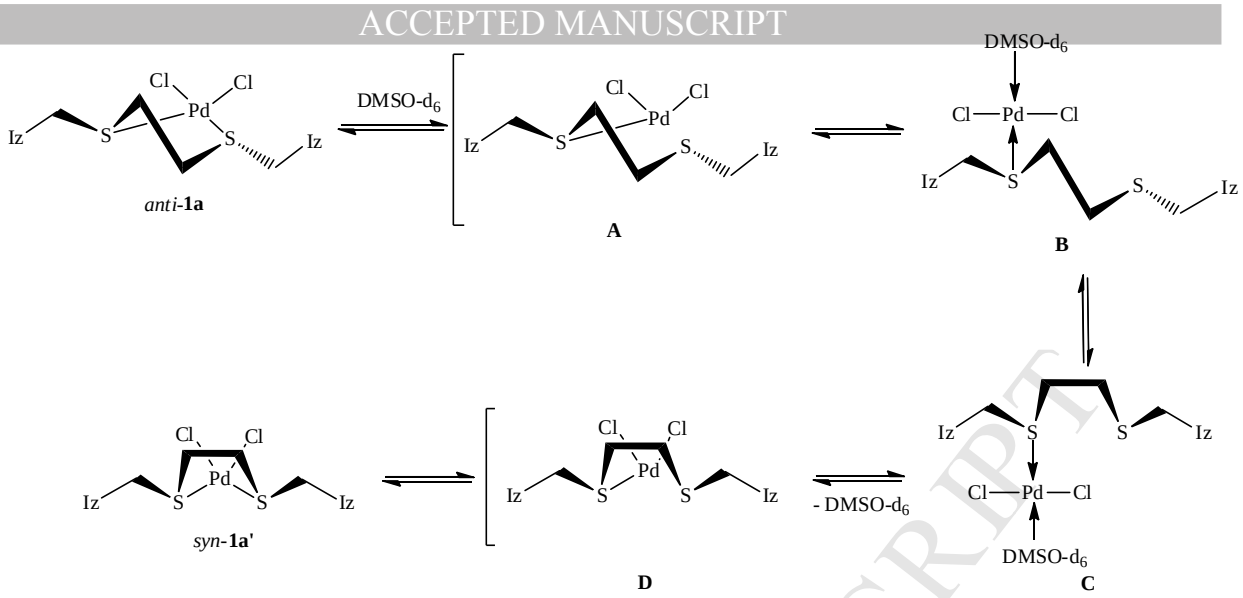


Fig. 2. Eyring plot for complex **1a**.

Positive values of entropy of activation of the exchange process of *anti*-**1a** in *syn*-**1a'** indicate isomerization through discontinuity of the coordination bond [15]. Obviously there is carried out discontinuity of S → Pd bond. As a consequence, in the NMR time scale the conformational change *anti*-**1a** to *syn*-**1a'** (Scheme 2) is observed via an open-chain intermediates in which the Pd atom coordinates DMSO through the hemilabile trigonal structure **A** [16a], affording the stable *trans*-dichloride Pd form **B** (1199 cm^{-1} see *Supplementary data*) [16b,c].

In the process of exchange between **B** and **C** there is a slow inversion about the sulfur atom [17]. Further transformation of **C** to *syn* **1a'** likely occurs via hemilabile intermediate **D**.



Scheme 2. Proposed mechanism of *anti*-**1a** in *syn*-**1a'** isomerization with participation of DMSO.

In this way, complex **1a** may be used like homogeneous Pd-catalyst due to its hemilabile behavior in solution.

A single crystal of palladaheterocycle **1a** was prepared via recrystallization from DMSO-d_6. X-ray data show that the asymmetric unit of crystal **1a** contains one by one molecule of DMSO-d_6 and compound **1a** (Fig. 3). Crystal-solvate **1a** crystallizes in the P-1 centrosymmetric triclinic space group with Z=2. 2,4-Dithiapalladacyclopentane adopts *twist* conformation, whereas dimethylisoxazole rings occupy *trans*-positions relative to it. The palladium atom is located in a four-coordinate planar environment. The Pd–Cl bond lengths are 2.315(10) and 2.321(10), whereas the Pd–S bond lengths are 2.249 (9) and 2.255(8) Å.

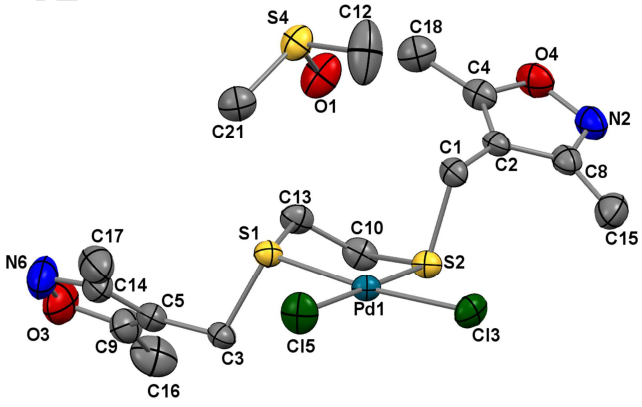


Fig. 3. ORTEP drawing of the crystal solvate of compound **1a** with DMSO in representation of the non-hydrogen atoms by thermal ellipsoids (p = 50%). Hydrogen atoms are omitted for clarity.

The Cl…H (CH_2), Cl…H (CH_3), and π…H (CH_3) non-covalent interactions in the crystal of **1a** lead to sheet structures along *a* crystallographic axis (Fig. 4). Two C–H…O (*1-x,1-y,1-z*) and one C–H…Cl (*2-x,1-y,-z*) hydrogen bonds are formed between DMSO-d_6 and **1a** molecules, and their lengths are 2.543(5) Å, 2.465(4) Å, and 2.805(4) Å, respectively

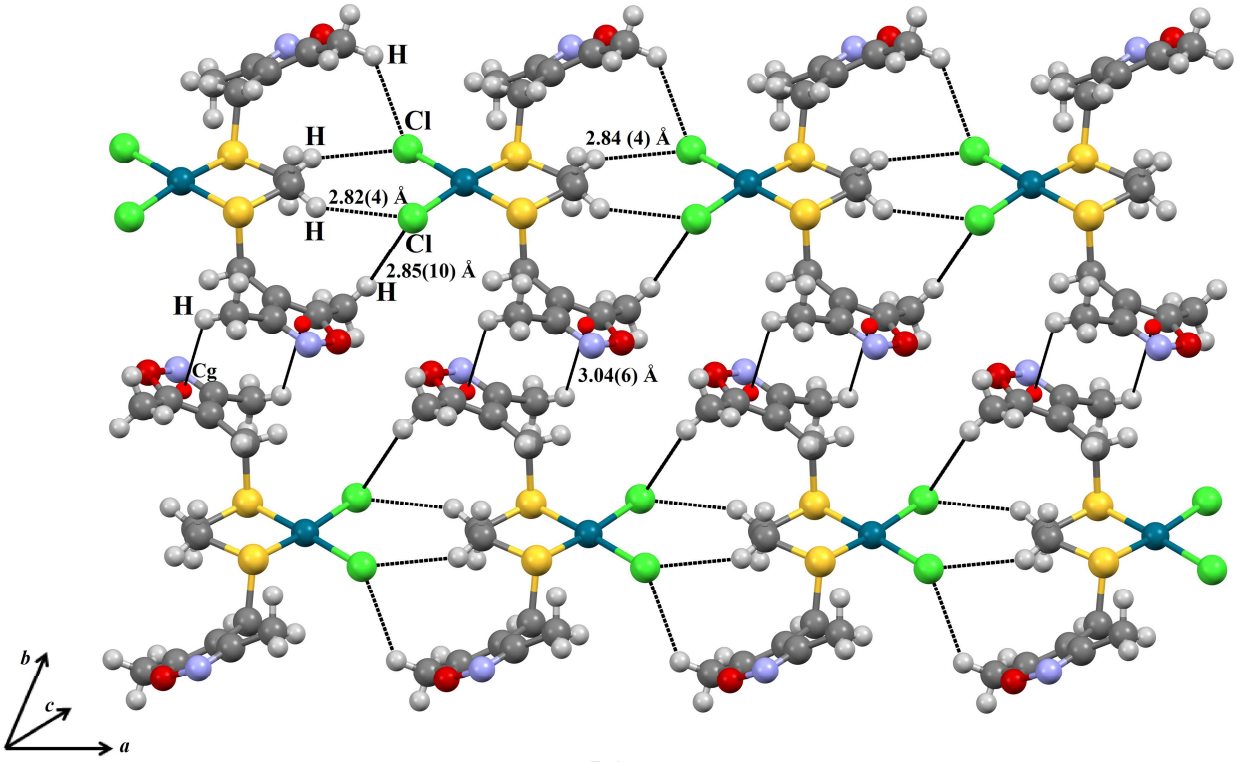


Fig. 4. Formation of sheet structures via C–H…Cl and CH…π interactions in **1a**

DMSO-d_6 molecules are in the cavities between sheets (Fig.5)

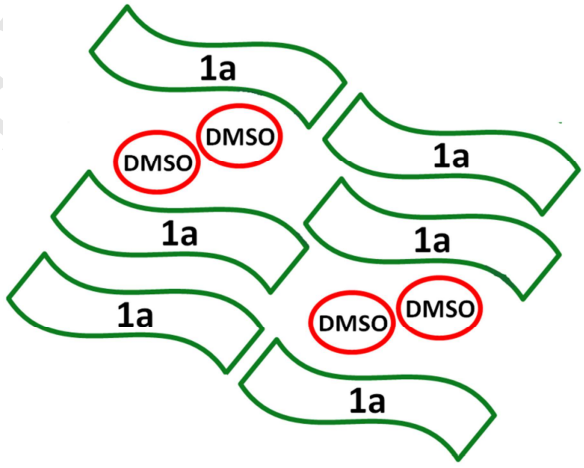
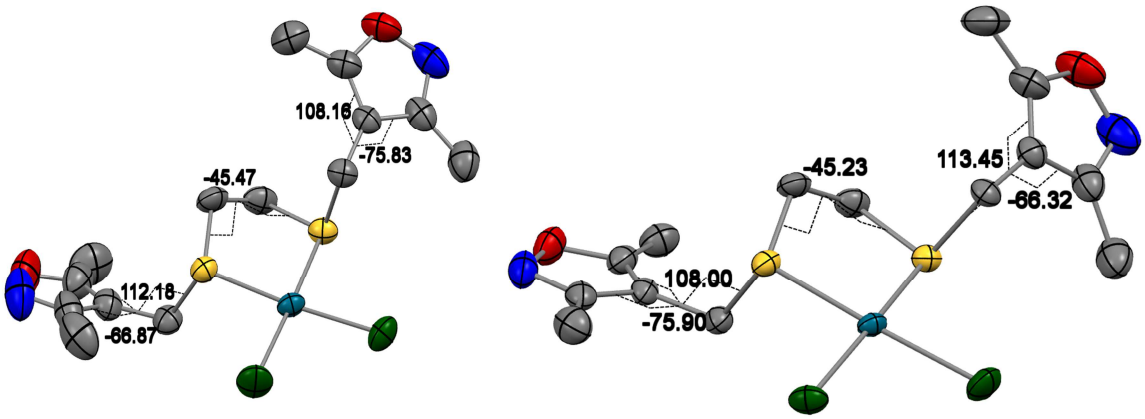


Fig. 5. Schematic representation of the packing of compound **1a** and DMSO-d_6 molecules in crystal

It should be added, minor rotation of isoxazole cycles is observed in the crystalline phase. Using X-ray diffraction low-temperature studies for **1a** show that this compound forms crystals

of a centrosymmetric type. The conformation of the dithiapalladacyclopentane ring practically remains unchanged at different temperatures. The rotation of one of the isoxazole cycles almost does not change, whereas the second isoxazole fragment changes its position by 1.27° at 200 K (Fig. 6).



T=298K T = 200 K

Fig. 6. ORTEP drawing of complex **1a** determined by X-ray analysis at 298 K and 200 K, with denoted the torsion angles. Hydrogen atoms are omitted for clarity.

As seen from the ^{1}H NMR spectra of palladium compounds **1a-d** (Fig. 7), the inversion speed of *anti*- and *syn*-isomers depends on their anionic orientation at the palladium atom. If the doublet-doublet system of IzCH_2S and SCH_2CH_2S fragments is observed in the acetate complex **1c** (Fig. 7) as a result of slow rotation like complex **1a**, then for complexes **1b** and **1d** the protons signals of the methylene and ethylene fragments merge into the broadened singlets even at room temperature. Obviously, the rotation of the sulfur atom in the recyclisation process of **1a-d** depends on steric and electronic factors and decreases in the following order: $Pd(NO_2)_2L \geq PdBr_2L > Pd(OAc)_2L > PdCl_2L$.

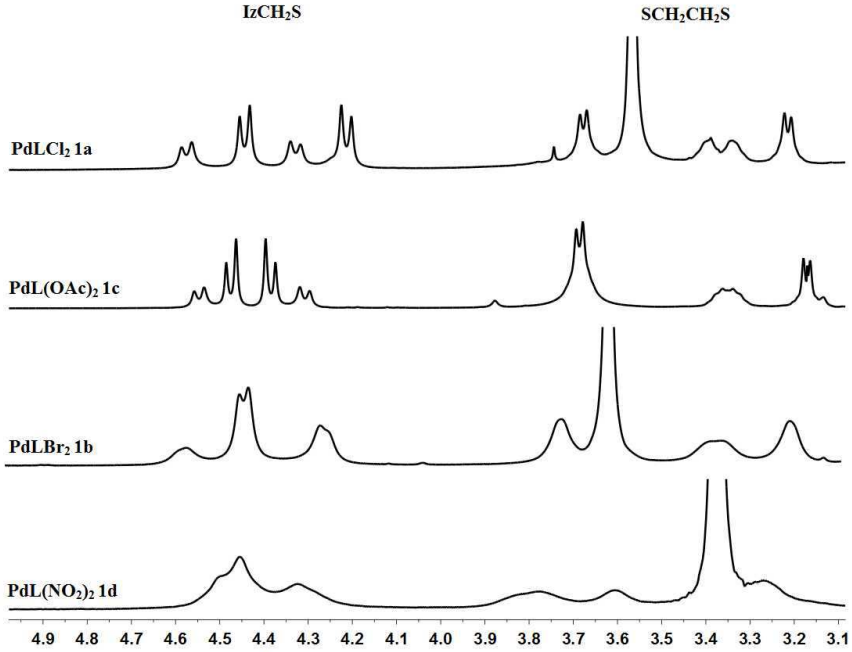


Fig. 7. Fragment of the ^{1}H NMR spectrum of an isomeric mixture of organopalladium compounds **1a-d** at room temperature

We failed to obtain MALDI-TOF mass spectra for the organic complexes of Pd(II) using HCCA and SA matrices due to the matrix-cluster formation. Similar results were reported in the literature by Petkovic [18]. However, mass spectra for **1a-d** had successfully obtained using electrospray ionization (ESI). For example, the intense molecular ion $[M+H]^+$ peak at *m/z* 537 was observed in the spectrum of complex **1c** (Fig. 8).

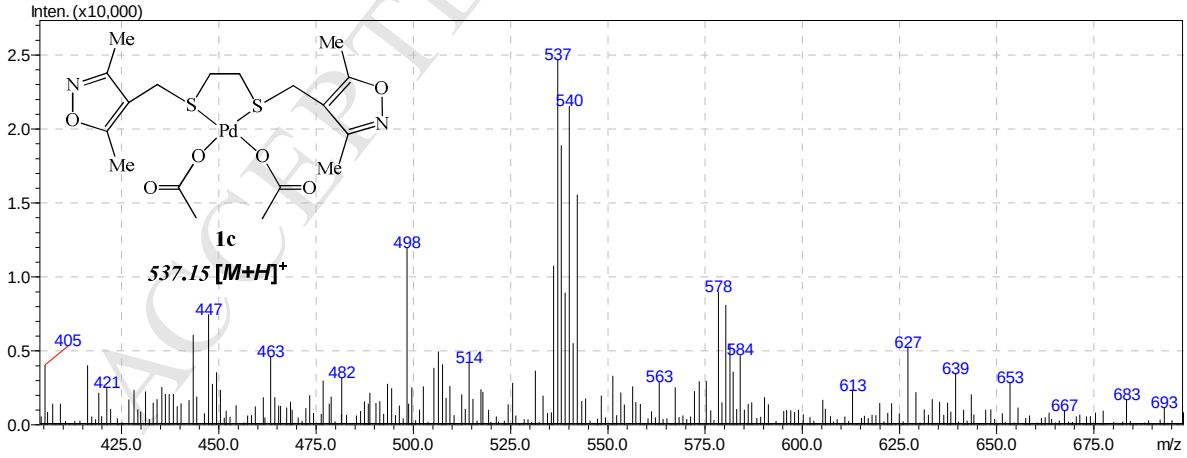


Fig. 8. The positive ion ESI mass spectrum of complex **1c**.

The most abundant peak of ion $[M+Cl–HNO_2]^-$ at *m/z* 498 was registered in the spectrum of complex **1d**. This ion forms due to a chlorine anion attachment to the analyte molecule from an eluent ($CHCl_3/CH_2Cl_2$) followed by the HNO_2 molecule elimination with retaining a negative charge on the residual fragment. In the case of compounds **1a** and **1b**, peaks of ions at *m/z* 523

$[M+Cl]^-$ and *m/z* 655 $[M+Br]^-$ (83% and 49% intensity, respectively) having specific isotope distribution were registered. Typically that the all peaks of isotopic distribution is complicated due to the presence of Pd-, Cl-, S-atoms (see *Supplementary data*).

Compound $PtCl_2$**L 2** is formed as a polycrystal. The *cis-S,S*-configuration of the platinacycle was suggested considering the presence of two very strong absorption bands at 332 and 322 cm^{-1} in the IR spectrum belonging to stretching vibrations of the *cis*-Pt-Cl bond [19]. The MALDI TOF/TOF spectrum also exhibits a molecular ion peak at *m/z* 615.936 $[M+K]^+$ (see *Supplementary data*).

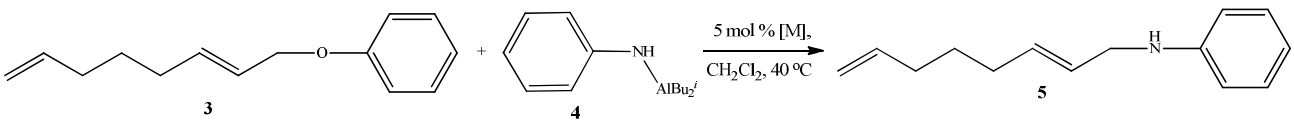
It is known that the salts K_2PtCl_4 and $PtCl_2$ coordinate S,S,N,N-containing reagents at the sulfur and nitrogen atoms to give mixtures of S,S-, S,N- and N,N-adducts [20]. However, in the case of N,O,S-containing ligand **L**, the Pd(II) and Pt(II) metal ions bind exclusively at the sulfanyl centers according to the HSAB principle (divalent S is a soft base) [21].

Catalytic reactivity of five-member Pd(II) and Pt(II) metallacycles ***1a-d, 2***

Synthesis of amines and their derivatives as universal building blocks in all chemical fields are widely used for the preparation of pharmaceuticals, fungicides, polymeric materials, selective sorbents, dyes, complexing agents, ion-exchange resins and many other products [22]. Taking into account the current trends to the intensification of environtmental processes, the catalytic activity of the synthesized metal containing compounds **1a-d** and **2** in the allylic amination reaction of 1-phenoxy-2,7-octadienyl **3** without the participation of a triphenylphosphine ligand was studied. Known that this reaction goes in the presence of the catalytic system $Pd(acac)_2$ – $2Ph_3P$ [23].

All our experiments were carried out in dichloromethane at 40 °C for 8 h and in the presence of 5 mol% catalyst (Table 1). Individual palladium salts having the triphenylphosphine ligand were also tested as catalysts. In the absence of the catalyst or in the presence of 5 mol% K_2PtCl_4 or $PtCl_2$**L 2a**, the reaction does not occur (Table 1, entries 1, 2, 12). Among the catalysts, the palladium (II) compound $PdCl_2$**L la** exhibited the greatest catalytic activity and demonstrated the highest yield (81%) of **5** (Table 1, entry 8), whereas the reaction between 2,7-octadienyl phenyl ether **3** and amide of aluminum **4** and 3 mol% $Pd(Ph_3P)_2Cl_2$ afforded **5** in 60% yield [24].

Table 1.
Effect of catalyst nature on the yield of 2,7-octadieny-l-phenyl-amine **5**[a]



3 4 5

Entry	Catalyst [M]	Yield of **5**, %	Entry	Catalyst [M]	Yield of **5**, %

1	–	–	7	$PdBr_2$	37
2	K_2PtCl_4	–	8	$PdCl_2$**L 1a**	81
3	$PdCl_2$	65	9	$PdBr_2$**L 1b**	45
4	$Pd(acac)_2$	62	10	Pd $(CH_3COO)_2$**L 1c**	50
5	$Pd(CH_3COO)_2$	63	11	Pd **(**$NO_2)_2$**L 1d**	43
6	$Pd(NO_3)_2 \cdot H_2O$	39	12	$PtCl_2$**L 2a**	–

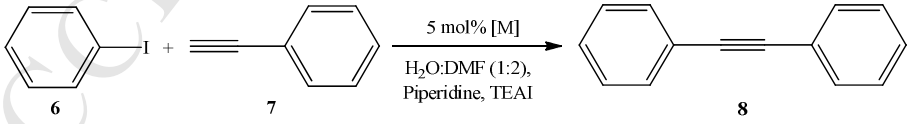
[a] Reaction conditions: CH_2Cl_2, 2,7-octadieny-l-phenyl ether **3** (2.2 mmol), aniline **4** (2.4 mmol), *i*-Bu_3Al (2.4 mmol), catalyst [M] (5 mol%), reaction duration 8 h, 40 °C, argon.

In continuation of investigations into the catalytic properties, complex **1a** was also tested in the palladium-catalyzed Sonogashira cross-coupling reaction. The usefulness of this reaction is that aryl alkynes are intermediates for the preparation of various important compounds ranging from natural products to pharmaceuticals [25a,b].

In recent years, one of the modifications of the Sonogashira cross-coupling reaction is based on using N,N- and C,N-palladaheterocycles as the catalysts without participation of the copper halide cocatalyst and triphenylphosphine as the ligand surrounding the palladium centre [26]. For the first time, we have carried out the Sonogashira reaction catalyzed by S,S-palladaheterocycle **1a**. The test reaction was carried out on the example of condensation between iodobenzene **6** and phenylacetylene **7** under selected conditions [26a] - in the presence of piperidine and triethylammonium iodide (TEAI) in DMF-water media.

It was found that when palladium (II) chloride was used as the catalyst, the yield of diphenylacetylene **8** was 68%, while the use of 5 mol% $PdCl_2$**L 1a** under similar conditions allowed to increase the yield of the target **8** to 79% (Table 2, entry 3). Increase in the reaction temperature to 100 °C led to 90 % yield of product **8** (Table 2, entry 4).

Table 2.
Effect of the reaction conditions (catalyst, solvent, temperature) on the yield of 1,2-diphenylethyne **8**[a]



6 **7** **8**

Entry	Catalyst [M]	Solvent	T, °C	Yield of **8**, %
1	–	H_2O : DMF (1:2)	100	–
2	$PdCl_2$	H_2O : DMF (1:2)	30	68
3	$PdCl_2$**L 1a**	H_2O : DMF (1:2)	30	79
4	$PdCl_2$**L 1a**	H_2O : DMF (1:2)	100	90
5	$PdCl_2$**L 1a**	DMF	100	56

6	$PdCl_2$**L 1a**	H_2O	100	54

[a]Reaction conditions: phenylacetylene **6** (1.2 mmol), iodobenzene **7** (1 mmol), solvent (6 mL), catalyst [M] (5 mol%), tetraethyl ammonium iodide (TEAI) (0.5 mmol), piperidine (2 mmol), reaction duration 4 h.

3. Conclusion

Thus, we have synthesized novel S,S-palladium(II) and platinum(II) heterocycles using polydentate N,O,S-containing ligand 1,2-bis(sulfanylmethyl-3,5-dimethylisoxazol-4-yl)ethane. It was determined that, in the solution, metallaheterocycles have inversion isomers – *anti* and *syn* forms via the recyclisation process. The dynamic 1H NMR was used to determine the coalescence temperature of exchange processes and the energy barrier of the isomerization, which amounted the activation enthalpy $\Delta H^{\neq}$ equal to 13.88 ± 0.6 kcal mol^{-1}, activation entropy $\Delta S^{\neq}$ 4.9 ± 1.6 cal mol^{-1} K^{-1} and the free energies of activation $\Delta G^{\neq}_{298}$ 12.4 ± 0.6 kcal mol^{-1}. Metallacyclic dichloro(3,5-dimethylisoxazol-4-yl)-1,2-dimethylsulfanylethane palladium(II) due to its hemilability was shown as an effective catalyst in the amination reaction of allyl phenyl ether with aniline and in the condensation reaction between phenylacetylene and iodobenzene**.**

4. Experimental

IR spectra were recorded on a Bruker Vertex-70V FTIR and Specord M80 spectrometers in suspension Nujol. UV spectra were recorded on a Perkin Elmer Lambda 750 UV/Vis spectrometer in $CHCl_3$ and DMSO over the wavelength range of 200–1000 nm, cuvette thickness 0.2 cm. ^1H and ^{13}C NMR spectra were acquired on Bruker Avance 400 (400 and 100 MHz, for compound **2**) and Bruker Ascend III HD 500 (500 and 125 MHz, respectively, for other compounds) spectrometers. The NMR spectrum of compounds (the $^{15}N–^1H$ HMBC experiment) was acquired on a Bruker Ascend 500 spectrometer (50 MHz). The solvent was DMSO-d_6, the internal standard for the ^1H and ^{13}C NMR spectra was TMS, for ^{15}N NMR spectra – urea (0.0 ppm). The homo- and heteronuclear 2D experiments were performed by the standard pulse sequences of Bruker. The variable-temperature (VT) ^1H NMR spectra of complex **1a** were measured in deuterated dimethyl sulfoxide (DMSO-d_6) in the temperature range of 293–373 K. Free activation energies were determined by the modified Eyring equation [27]. Electron ionization (70 eV) spectrum of compound **1a-d** was obtained on a Finnigan 4021 gas chromatography-mass spectrometer (HP-5 glass capillary column, 50.000×0.25 mm; carrier gas helium; oven temperature programming from 50 to 300 °C at a rate of 0.1 °/min; injector temperature 280 °C; ion source temperature 250 °C). Electrospray ionization (ESI) mass spectra were obtained on a HPLC mass spectrometer LCMS-2010EV (Shimadzu) in the positive and negative ions mode at the ionizing electrode potential of 4.5 kV and −3.5 kV, respectively. Sample solution (direct syringe sample inlet) was in methanol (acetonitrile), mobile phase

(acetonitrile/water, 95:5) flow rate was 0.1 mL/min. The heater's and the desolvation line's temperature was 200 and 230 °C, respectively. The nebulizer gas (nitrogen) flow rate was 1.5 L/min. Matrix-assisted laser desorption/ionization (MALDI) mass spectrum was recorded on a Bruker's device MALDI TOF Autoflex III (complex **2** in DMSO) with sinapinic acid as a matrix (see *Supplementary data*). Mass spectra of compounds **5**, **8** were recorded on a gas chromatography-mass spectrometer Shimadzu GC-MS 2010 QP2010 Ultra, (GC-MS-QP2010 Ultra, capillary column Supelco 5 ms, 60 m×0.25 mm×0.25 mcm). Elemental analysis was performed on a Karlo Erba 1106 elemental analyzer. Melting points were determined on a Kofler hot-stage microscope and utilized uncorrected. Synthesis of 1,2-*bis*(3,5-dimethylisoxazol-4-yl-methylsulfanyl)ethane **L** was carried out according to the procedure described previously [11].

4.1. Syntheses

*4.1.1. Synthesis of the syn-, anti-isomeric mixture of dichloro(3,5-dimethylisoxazol-4-yl)-1,2-dimethylsulfanylethane palladium(II) **(1a)***. Palladium chloride(II) (0.24 g, 1.41 mmol) was dissolved in acetonitrile (15 mL) with stirring at 60 °C in the glass vessel. Then 1,2-*bis*(3,5-dimethylisoxazol-4-yl-methylsulfanyl)ethane (0.44 g, 1.41 mmol) was added and stirred at room temperature (~ 20 °C) for 3 h. The resulting bright yellow precipitate was filtered through filter paper (blue ribbon) and washed by acetonitrile (30 mL), water (30 mL) and dried in air without heat to obtain complex ***(1a)***, (0.37 g, 54%), yellow powder; [Found: C, 34.19; H, 4.04; Cl, 14.62; N, 5.83; Pd, 21.94, S, 13.14. $C_{14}H_{20}Cl_2N_2O_2PdS_2$ calculated C, 34.33; H, 4.12; Cl, 14.48; N, 5.72; Pd, 21.73; S, 13.09]; ν_{max}(Nujol): 1635 (br), 1274, 1250, 1193, 883, 829, 715, 661, 334 (br), 307 cm^{-1}; λ_{max} (DMSO) 395 nm; δ_H (400 MHz, DMSO-d_6) 4.63 (2H, dd, ^2J 14.4, Hz, IzC$\underline{H_2}$S), 4.33 (2H, dd, ^2J 14.4 Hz, IzC$\underline{H_2}$S), 4.47 (2H, dd, ^2J 14.0 Hz, IzC$\underline{H_2}$S), 4.18 (2H, dd, ^2J 14.0 Hz, IzC$\underline{H_2}$S), 3.51 (2H, dd, ^2J = 9.2 Hz, SCH_2CH_2S), 3.15 and 3.09 (2H, br s, CH_2, SCH_2CH_2S), 2.93 (2H, dd, ^2J = 9.2 Hz, SCH_2CH_2S), 2.43 (6H, s, Me), 2.26 (6H, s, Me); δ_C (500 MHz, DMSO-d_6) 168.9, 159.6, 107.8, 37.5 and 37.3 (*syn*- and *anti*-isomers), 30.4 and 29.7 (*syn*- and *anti*-isomers), 11.5, 10.3; δ_N (500 MHz, DMSO-d_6) 370.9; ESI, *m/z* (%): 523 (87) $[M+Cl]^-$. $C_{14}H_{20}Cl_3N_2O_2PdS_2$ 523;

*4.1.2. Dibromo(3,5-dimethylisoxazol-4-yl)-1,2-dimethylsulfanylethane palladium(II) **(1b)***, (0.66 g, 81%), yellow powder; [Found: C, 29.24; H, 3.43; Br, 27.85; N, 4.51; Pd, 18.33, S, 11.46. $C_{14}H_{20}Br_2N_2O_2PdS_2$ calculated C, 29.06; H, 3.48; Br, 27.62; N, 4.84; Pd, 18.39; S, 11.08]; ν_{max}(Nujol): 1623 (br), 1197, 1032, 737, 721, 576, 340, 326, 300, 283 cm^{-1}; λ_{max} (DMSO) 301 nm; δ_H (400 MHz, DMSO-d_6) 4.60 (2H, br s, IzC$\underline{H_2}$S), 4.22 (2H, br s, IzC$\underline{H_2}$S), 4.44 (2H, d, ^2J 12.5 Hz, IzC$\underline{H_2}$S), 3.53 (2H, br s, SCH_2CH_2S), 3.10 and 3.07 (2H, d, ^2J 16.5 Hz, CH_2, SCH_2CH_2S), 2.88 (2H, s, SCH_2CH_2S), 2.43 (6H, s, Me), 2.26 (6H, s, Me); δ_C (500 MHz, DMSO-

d_6) 168.9, 159.6, 108.1, 38.2, 37.8, 30.9, 29.7, 11.5, 10.4; δ_N (500 MHz, DMSO-d_6) 370.4; ESI, m/z (%): 655 (49) $[M+Br]^-$. $C_{14}H_{20}Br_3N_2O_2PdS_2$ 655;

4.1.3. Diacetate(3,5-dimethylisoxazol-4-yl)-1,2-dimethylsulfanylethane palladium(II) ***(1c)***, (0.55 g, 73%), powder light yellow; [Found: C, 40.08; H, 5.31; N, 5.26; Pd, 19.71, S, 12.14. $C_{18}H_{26}N_2O_6PdS_2$ calculated C, 40.26; H, 4.88; N, 5.22; Pd, 19.82; S, 11.94]; ν_{max}(Nujol): 3401, 1621, 1589, 1312, 1198, 1038; 721, 680, 328 (br), 294, 281 cm^{-1}; λ_{max} ($CHCl_3$) 371 nm; δ_H (400 MHz, DMSO-d_6) 4.46 (2H, dd, ^2J 14.0, Hz, IzC$\underline{H_2}$S), 4.15 (2H, dd, ^2J 14.0 Hz, IzC$\underline{H_2}$S), 4.37 (2H, dd, ^2J 14.5 Hz, IzC$\underline{H_2}$S), 4.25 (2H, dd, ^2J 14.0 Hz, IzC$\underline{H_2}$S), 3.35 (2H, dd, ^2J = 9.5 Hz, SCH_2CH_2S), 2.92 (2H, ^2J 14.5 Hz, CH_2, SCH_2CH_2S), 2.69 (2H, dd, ^2J = 9.5 Hz, SCH_2CH_2S), 2.43 (6H, s, Me), 2.22 (6H, s, Me), 1.77 (6H, s, Me); δ_C (500 MHz, DMSO-d_6) 175.4, 168.9, 159.7, 107.8, 35.2, 34.9, 29.4, 28.9, 23.2, 11.3, 10.1; δ_N (500 MHz, DMSO-d_6) 370.4; ESI, m/z (%): 537 (100) $[M+H]^+$. $C_{18}H_{27}N_2O_6PdS_2$ 537;

4.1.4. Dinitro(3,5-dimethylisoxazol-4-yl)-1,2-dimethylsulfanylethane palladium(II) ***(1d)***, (0.53 g, 74%), light brown powder; Found: C, 33.12; H, 3.91; N, 10.84; Pd, 20.94, S, 12.61. $C_{14}H_{20}N_4O_6PdS_2$ calculated C, 32.91; H, 3.95; N, 10.97; Pd, 20.83; S, 12.55]; ν_{max}(Nujol): 1627 (br), 1199, 1038; 884, 730, 711, 483, 384, 309, 282 cm^{-1}; λ_{max} (DMSO) 309 nm; δ_H (400 MHz, DMSO-d_6) 4.45 (2H, br s, IzC$\underline{H_2}$S), 4.33 (2H, br s, IzC$\underline{H_2}$S), 3.51 (2H, dd, ^2J = 9.2 Hz, SCH_2CH_2S), 3.76, 3.60, 3.27 (2H, br s, CH_2, SCH_2CH_2S), 2.93 (2H, dd, ^2J = 9.2 Hz, SCH_2CH_2S), 2.53 (6H, s, Me), 2.30 (6H, s, Me); δ_C (500 MHz, DMSO-d_6) 169.9, 159.8, 106.8, 36.4, 31.4, 30.1, 11.4, 10.1; δ_N (500 MHz, DMSO-d_6) 370.0; ESI, m/z (%): 498 (100) $[M+Cl–HNO_2]^-$. $C_{14}H_{19}ClN_3O_4PdS_2$ 498. $C_{14}H_{20}N_4O_6PdS_2$ 510.

4.1.5. Synthesis of dichloro(3,5-dimethylisoxazol-4-yl)-1,2-dimethylsulfanylethane platinum(II) ***(2)***. Potassium tetrachloroplatinate (0.23 g, 0.56 mmol) was dissolved of water (5 mL) at room temperature (~ 20 °C) in the glass vessel and stirring vigorously on a magnetic stirrer, a solution of 1,2-*bis*(3,5-dimethylisoxazol-4-yl-methylsulfanyl)ethane (0.17 g, 0.56 mmol) in acetone (10 mL) was added. The mixture was stirred for 3 h, then evaporated with gentle heating acetone. The resulting precipitate was washed with water, hexane and air-dried to give complex **2** (0.28 g, 86 %), bright yellow powder; [Found: C, 29.20; H, 3.42; Cl, 11.88; N, 4.70; Pt, 33.96, S, 11.22. $C_{14}H_{20}Cl_2N_2O_2PtS_2$ calculated C, 29.07; H, 3.49; Cl, 12.26; N, 4.84; Pt, 33.73, S, 11.09]; ν_{max}(Nujol): 1635, 1275, 1249, 1203, 883, 747, 714, 322, 322 (br) cm^{-1}; λ_{max} (DMSO) 290, 366 nm; $_H$ (400 MHz, DMSO-d_6) 4.51 (2H, dd, ^2J 14.4 Hz, IzC$\underline{H_2}$S), 4.32 (2H, dd, ^2J 14.4 Hz, IzC$\underline{H_2}$S), 4.34 (2H, dd, ^2J 14.0 Hz, IzC$\underline{H_2}$S), 4.04 (2H, dd, ^2J 14.0 Hz, IzC$\underline{H_2}$S); 2.83 (2H, dd, ^2J = 10.0 Hz, SCH_2CH_2S), 3.39 (2H, dd, ^2J = 10.0 Hz, SCH_2CH_2S); 3.01 and 3.00 (2H, br s, CH_2, SCH_2CH_2S), 2.44 (6H, s, Me); 2.27 (6H, s, Me); δ_C (500 MHz, DMSO-d_6) 168.9,

159.6, 107.9, 107.8, 37.9, 37.7, 30.5, 29.6, 11.6, 10.4; δ_N (500 MHz, DMSO-d_6) 369.9; MALDI TOF: $[M+K]^+$ found 615.936. $C_{14}H_{20}Cl_2KN_2O_2PtS_2$ requires 615.962.

4.2. Catalytic activity measurement

4.2.1. Synthesis of (E)-N-(octa-2,7-dien-1-yl)aniline (5). To a solution of aniline (1.09 mL, 12 mmol) in CH_2Cl_2 (10 mL) at 0 °C under argon was added dropwise *i*-Bu_3Al (3.48 mL, 12 mmol), stirred for 1 h at 40 °C until the evolution of gas has stopped, cooled to 0 °C (ice bath). Then 5 mol% of the catalyst and 1,4-phenoxy-2,7-octadiene (2.02 g, 10 mmol) were added. The mixture was stirred for 8 h at 40 °C. Then saturated NH_4Cl solution (30 mL) was added. Product was extracted with ethyl acetate (3 × 15 mL). The organic layer was dried with $MgSO_4$ and concentrated. The purity of the obtained (E)-N-(octa-2,7-dien-1-yl)aniline was checked by GC and GC-MS [19].

*4.2.1.1. (E)-N-(octa-2,7-dien-1-yl)aniline (**5**).* (1.81 g, 90%) Oil, GC–MS, m/z (relative intensity): 201 (25), 132 (45), 106 (30), 93 (100), 55 (20). $C_{14}H_{19}N$ requires 201.152.

*4.2.2. Synthesis of 1,2-diphenylethyne (**8**). Synthesis of 1,2-diphenylethyne using complex **1a** as the catalyst was carried out according to the procedure [26a].*

Under argon atmosphere, a mixture of phenylacetylene (0.13 mL, 1.2 mmol), iodobenzene (0.11 mL, 1 mmol), catalyst (5 mol%), TEAI (0.13 g, 0.5 mmol), piperidine (0.2 mL, 2.0 mmol) in H_2O:DMF (1:2, 6.0 mL) solvent was stirred for 4 h at a temperature of 100 °C . Than the mixture was cooled to room temperature and was extracted with EtOAc (2 × 10). The combined organic phases dried over anhydrous $MgSO_4$, and concentrated. The purity of the obtained 1,2-diphenylethyne was checked by GC and GC-MS.

*4.2.2.1. 1,2-diphenylethyne (**8**).* Powder, m.p. 58 – 60 °C (lit. [28] 60–61 °C), GC–MS m/z (relative intensity): 178 (100), 152 (12), 126 (10), 89 (18), 76 (22), 63 (12). $C_{14}H_{10}$ requires 178.229 [29].

4.3. X-ray crystallography

X-ray diffraction data of single-crystal **1a** was collected on a XCalibur Eos diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Collection and processing of data performed with using the program CrysAlis^{Pro} Oxford Diffraction Ltd. The structure was solved by direct methods as implemented in the program SHELXS. The refinement was carried out using SHELXL [30]. The structure was refined by a full-matrix least-square technique using anisotropic thermal parameters for non-hydrogen atoms and a riding model for hydrogen atoms. Crystal structure was generated by Mercury [31]. Atomic coordinates, bond lengths, bond angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data

Centre (www.ccdc.cam.ac.uk/data_request/cif). The crystallographic data for compounds **1a** and **1a′** are collected in Table 3.

Table 3.
Crystal data and structure refinement for **1a**

Empirical formula	$C_{14}H_{20}Cl_2N_2O_2PdS_2$	
Formula weight	489.95	
Temperature, K	298(2)	200(2)
Crystal system	triclinic	
Space group	P-1	
a, Å	8.1977(3)	8.2024(4)
b, Å	12.5793(7)	12.4593(6)
c, Å	13.5209(8)	13.4254(7)
α, °	63.182(6)	63.440(5)
β, °	72.378(4)	72.406(5)
γ, °	79.084(4)	79.680(4)
Volume, $Å^3$	1183.67 (13)	1168.27 (10)
Z	2	2
$\rho_{calc,}$ g/cm^3	1.593	1.614
Radiation	MoKα (λ = 0.71073)	
Reflections collected	9983	11589
Independent reflections	5435 (R_{int} = 0.0142)	6499 (R_{int} = 0.0464)
Goodness-of-fit on F^2	0.848	0.625
Final R indexes [I>=2σ (I)]	R_1 = 0.0299, wR_2 = 0.0962	R1 = 0.0373, wR2 = 0.0894
Final R indexes [all data]	R_1 = 0.0412, wR_2 = 0.1141	R1 = 0.0756, wR2 = 0.1146
CCDC №	1558122	1011993

5. Supplementary material

Supplementary data related to this article can be found at http://dx.doi.org/.

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The structural studies of new compounds were performed on the equipment available at the "Agidel" and "Khimiya" centres for Collective Use.

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In this research we obtained following highlights:

– Novel Pd(II) and Pt(II) metallaheterocycles were synthesized

– Five-membered S,S-palladacycle is in the *twist*-conformation with *trans*-isoxazole rings (x-ray diffraction)

– Proposed mechanism of *anti- syn-* isomerization of palladacycle via an open-chain forms was offered

– The activation energy $\Delta H^{\neq}$, $\Delta S^{\neq}$ and rate of reversible *anti-syn* isomerization were established by dynamic NMR

– Hemilabile palladaheterocycle is an effective catalyst in the amination and Sonogashira reactions