

Naphthalimide-based platinum(II) and palladium(II) N-heterocyclic carbene complexes: synthesis and structural elucidation

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Dedicated to Acad. Bogdan Kurtev on the occasion of his 100th birth anniversary

The synthesis and characterization of five catalytically relevant Pd(II) and Pt(II) complexes involving N-heterocyclic carbenes (NHCs) derived from substituted 1,8-naphthalimides and σ -donor neutral monodentate ligands (DMSO, PPh₃, C₆H₅N and 4-dimethylaminopyridine (DMAP)) is reported. The structure and configuration of the complexes were elucidated on the basis of combination of NMR and DFT studies.

Key words: NHC complexes; ¹H, ¹³C and ¹⁹⁵Pt NMR spectroscopy; DFT calculations

INTRODUCTION

The discovery of N-heterocyclic carbenes (NHCs) by Wanzlick [1–3] and Öfele [4] in the 1960s attracted a significant attention to stable NHCs [5–7] as ancillary ligands in various transition-metal-mediated catalytic reactions such as olefin metathesis [8–10], Pd-catalyzed cross-coupling reactions [11–14] and hydrogenation reactions [15–17]. PEPPSI-typed (Pyridine Enhanced Precatalyst Preparation, Stabilization, and Initiation) complexes are one of the most fertile and well-performed catalysts in various C-C coupling reactions [18, 19]. Recently, Pt(II)-NHC complexes, exceeding their Pt(0) counterparts in air- and moisture-stability, have been increasingly used in homogeneous catalysis especially in hydrosilylation reaction [20–22]. N-heterocyclic carbenes are characterized as strong σ -donors, even stronger than alkyl phosphines; their steric properties are also entirely different than those of phosphines. NHCs also represent less severe environmental risks associated with phosphorus compounds. These advantages define them as favorable ligands for catalysis as well as precatalysts.

1,8-naphthalimide system and its derivatives demonstrate attractive electronic and photoactive properties, their respective fluorescent compounds serve as chemosensors for cations [23, 24],

biosensors [25], optoelectronic materials [26]. 4-amino-3-nitro-1,8-naphthalimides and their 3,4-diamino derivatives as starting compounds for preparation of N-heterocyclic carbene precursors were recently reported by us and their spectroscopic properties were studied [27, 28]. Fusion of imidazole-2-ylidenes to 1,8-naphthalimide moiety to a naphthalimide core affects the aromatic system, providing further attractive features and interesting photo-physical applications of their organometallic complexes. As part of our current interest in carbene complexes, herein we report the synthesis and structural elucidation of new Pt(II) NHC complexes and a palladium PEPPSI-motif complex derived from 5,10-dibutyl-8-(4-methylbenzyl)-4,6-dioxo-4,5,6,10-tetrahydrobenzo[*de*]imidazo[4,5-*g*]isoquinolin-8-ium chloride, *NHC.HCl*, which provide grounds for comparison of metal influences on the spectroscopic properties of the imidazo-naphthalimide ligand system.

EXPERIMENTAL

All reagents purchased from commercial suppliers were used without any further purification. Starting compounds *cis*-[Pt(DMSO)₂(Cl)₂] [29], *trans*-[Pd(Pyr)₂(Cl)₂] [30] and the NHC ligand [28, 31] were prepared according to literature procedures. All of the reactions were performed under inert atmosphere (Ar) using standard Schlenk techniques. The NMR spectra were recorded on a Bruker Avance II+ 600 (600.13 for ¹H NMR, 150.92 MHz for ¹³C NMR,

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242.92 MHz for ^{31}P NMR and 129.01 MHz for ^{195}Pt NMR), spectrometer with TMS (85% H_3PO_4 for ^{31}P) as internal standard for proton and carbon chemical shifts (δ , ppm). ^{195}Pt NMR spectra are referred to the signal of 1.2M Na_2PtCl_6 in D_2O . ^1H and ^{13}C NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants J (Hz), integration and identification. The assignment of the ^1H and ^{13}C NMR spectra was made on the basis of DEPT, COSY, HSQC, HMBC and NOESY experiments. Flash chromatography was performed on Silica Gel 60 (0.040–0.063 nm). Elemental analyses were performed by Microanalytical Service Laboratory of Faculty of Chemistry and Pharmacy, University of Sofia, using Vario EL3 CHNS(O) and Microanalytical service Laboratory of the Institute of Organic Chemistry, Bulgarian Academy of Science.

The DFT calculations were carried out on MADARA cluster (<http://madara.orgchm.bas.bg>) using program package GAUSSIAN 09 [32]. Geometry optimizations were performed by using density functional theory [33–35] with B3LYP functionals [36, 37]. As for the basis sets, we used 6-31G(d) sets for C, H, N, O, S, P and Cl [37]. For Pd and Pt, we used LANL2DZ basis sets [38], whose core parts were represented by effective core potentials (ECP). Solvent was included implicitly to the optimizations via the SMD [39] model with the built in solvent parameters. The nature of all critical points was confirmed by means of the vibrational analysis, and ZPV energies were evaluated. The thermal and entropy corrections to Gibbs free energy to 298.15 K have been calculated for all minima from unscaled vibrational frequencies obtained at the same level.

Synthesis of *trans*-[(NHC)Pd(Pyr)(Cl)₂], complex 1:

A Schlenk tube was charged with a magnetic stir bar, **NHC.HCl** (100 mg, 0.2 mmol), **trans**-[Pd(Pyr)₂(Cl)₂] (75 mg, 1.1 eqv.), 2 ml dry THF and finely powdered freshly dried K_2CO_3 (56 mg, 2 eqv.). The mixture was stirred for 2 hours at 40 °C and after cooling to room temperature, the reaction mixture was filtered through a pad of Celite and washed with DCM until the entire product was eluted. After evaporation of all volatiles the product was purified by column chromatography, eluting with petroleum ether/acetone = 4:1. Yield: 90 mg (63%) of pale yellow solid with m.p. decomposition over 120 °C. ^1H NMR (600 MHz, CDCl_3) δ = 0.968

(t, J = 7.4 Hz, 3H, **CH**₃-5-*n*-Bu), 1.204 (t, J = 7.4 Hz, 3H, **CH**₃-10-*n*-Bu), 1.401-1.463 (m, 2H, **CH**₂CH₃-5-*n*-Bu), 1.666-1.717 (m, 2H, **CH**₂CH₂CH₃-5-*n*-Bu), 1.792-1.854 (m, 2H, **CH**₂CH₃-10-*n*-Bu), 2.318 (s, 3H, **CH**₃-*p*-xylyl), 2.301-2.361 (m, 2H, **CH**₂CH₂CH₃-10-*n*-Bu), 4.128-4.154 (m, 2H, **NCH**₂-5-*n*-Bu), 5.546-5.575 (m, 2H, **NCH**₂-10-*n*-Bu), 6.374 (s, 2H, **NCH**₂-*p*-xylyl), 7.189 (d, J = 8.0 Hz, 2H, **H**3,5-*p*-xylyl), 7.402-7.425 (m, 2H, **H**3,5-pyr), 7.559 (d, J = 8.0 Hz, 2H, **H**2,6-*p*-xylyl), 7.827 (dd, J = 1.6, 7.6 Hz, 1H, **H**4-pyr), 7.958 (dd, J = 7.4, 8.5 Hz, 1H, **H**2-naphthyl), 8.508 (s, 1H, **H**7-naphthyl), 8.621 (dd, J = 0.8, 8.5 Hz, 1H, **H**1-naphthyl), 8.687 (dd, J = 0.8, 7.4 Hz, 1H, **H**3-naphthyl), 9.026-9.041 (m, 2H, **H**2,6-pyr). ^{13}C NMR (151 MHz, CDCl_3) δ = 13.84 (**CH**₃-5-*n*-Bu), 13.92 (**CH**₃-10-*n*-Bu), 20.25 (**CH**₂CH₃-5-*n*-Bu), 20.40 (**CH**₂CH₃-10-*n*-Bu), 21.24 (**CH**₃-*p*-xylyl), 30.10 (**CH**₂CH₂CH₃-5-*n*-Bu), 31.17 (**CH**₂CH₂CH₃-10-*n*-Bu), 40.66 (**NCH**₂-5-*n*-Bu), 51.60 (**NCH**₂-10-*n*-Bu), 53.47 (**NCH**₂-*p*-xylyl), 116.62 (**C**7-naphthyl), 119.02 (**Ar**-⁴C), 123.74 (**Ar**-⁴C), 124.68 (**Ar**-⁴C), 124.71 (**C**3,5-pyr), 125.63 (**Ar**-⁴C), 126.74 (**C**1-naphthyl), 127.91 (**C**2,6-*p*-xylyl), 128.18 (**C**2-naphthyl), 129.88 (**C**3,5-*p*-xylyl), 130.17 (**C**3-naphthyl), 131.33 (**Ar**-⁴C), 132.44 (**Ar**-⁴C), 132.54 (**Ar**-⁴C), 138.39 (**C**4-pyr), 138.44 (**Ar**-⁴C), 151.32 (**C**2,6-pyr), 163.30 (⁴**C**6-carbonyl), 163.82 (⁴**C**4-carbonyl), 166.85 (⁴**C**_{NHC}). $\text{C}_{34}\text{H}_{36}\text{Cl}_2\text{N}_4\text{O}_2\text{Pd}$: calcd. C, 57.52; H, 5.11; N, 7.89; found: C, 57.60; H, 5.12; N, 7.63.

Synthesis of *cis*-[(NHC)Pt(DMSO)(Cl)₂], complex 2:

A Schlenk tube was charged with a magnetic stir bar, **NHC.HCl** (250 mg, 0.51 mmol), *cis*-[Pt(DMSO)₂(Cl)₂] (240 mg, 1.1 eqv.), 2 ml dry THF and finely powdered freshly dried K_2CO_3 (140 mg, 2 eqv.). The mixture was stirred for 18 hours at 40 °C and after cooling to room temperature, the reaction mixture was filtered through a pad of Celite and washed with DCM until the entire product was eluted. After evaporation of all volatiles the product was purified by column chromatography, eluting with DCM /ethyl acetate = 4:1. Yield: 350 mg (88%) of pale yellow solid with m.p. decomposition over 120 °C: ^1H NMR (600 MHz, CDCl_3) δ = 0.953 (t, J = 7.4 Hz, 3H, **CH**₃-5-*n*-Bu), 1.139 (t, J = 7.4 Hz, 3H, **CH**₃-10-*n*-Bu), 1.382-1.453 (m, 2H, **CH**₂CH₃-5-*n*-Bu), 1.652-1.701 (m, 2H, **CH**₂CH₂CH₃-5-*n*-Bu), 1.731-1.791 (m, 2H, **CH**₂CH₃-10-*n*-Bu), 2.045-2.131 (m, 1H, a-**CH**₂CH₂CH₃-10-*n*-Bu), 2.267-2.347 (m, 1H, b-

$\text{CH}_2\text{CH}_2\text{CH}_3$ -10-*n*-Bu), 2.305 (s, 3H, CH_3 -*p*-xylyl), 2.981 (s, 3H, CH_3 -DMSO), 3.537 (s, 3H, CH_3 -DMSO), 4.132-4.157 (m, 2H, NCH_2 -5-*n*-Bu), 5.221-5.272 (m, 1H, a- NCH_2 -10-*n*-Bu), 5.333-5.381 (m, 1H, b- NCH_2 -10-*n*-Bu), 5.933 (d, $J = 16.3$ Hz, 1H, a- NCH_2 -*p*-xylyl), 6.478 (d, $J = 16.3$ Hz, 1H, b- NCH_2 -*p*-xylyl), 7.152 (d, $J = 8.2$ Hz, 2H, **H2,6**-*p*-xylyl), 7.212 (d, $J = 8.2$ Hz, 2H, **H3,5**-*p*-xylyl), 7.993 (dd, $J = 7.4, 8.6$ Hz, 1H, **H2**-naphthyl), 8.575 (s, 1H, **H7**-naphthyl), 8.591 (dd, $J = 0.7, 8.6$ Hz, 1H, **H1**-naphthyl), 8.707 (dd, $J = 0.7, 7.4$ Hz, 1H, **H3**-naphthyl). ^{13}C NMR (151 MHz, CDCl_3) $\delta = 13.75$ (CH_3 -5-*n*-Bu), 13.83 (CH_3 -10-*n*-Bu), 20.17 (CH_2CH_3 -10-*n*-Bu), 20.28 (CH_2CH_3 -5-*n*-Bu), 21.08 (CH_3 -*p*-xylyl), 30.01 ($\text{CH}_2\text{CH}_2\text{CH}_3$ -5-*n*-Bu), 30.73 ($\text{CH}_2\text{CH}_2\text{CH}_3$ -10-*n*-Bu), 40.58 (NCH_2 -5-*n*-Bu), 45.21 (CH_3 -DMSO), 45.86 (CH_3 -DMSO), 51.67 (NCH_2 -10-*n*-Bu), 52.06 (NCH_2 -*p*-xylyl), 116.57 (**C7**-naphthyl), 119.41 (**Ar**- ^{13}C), 120.00 (**Ar**- ^{13}C), 123.83 (**Ar**- ^{13}C), 126.01 (**Ar**- ^{13}C), 126.70 (**C1**-naphthyl), 126.89 (**C3,5**-*p*-xylyl), 128.41 (**C2**-naphthyl), 129.87 (**C2,6**-*p*-xylyl), 130.29 (**C3**-naphthyl), 131.11 (**Ar**- ^{13}C), 131.26 (**Ar**- ^{13}C), 132.24 (**Ar**- ^{13}C), 138.40 (**Ar**- ^{13}C), 158.16 ($^{13}\text{C}_{\text{NHC}}$), 163.05 ($^{13}\text{C}_{\text{C4}}$ -carbonyl), 163.60 ($^{13}\text{C}_{\text{C6}}$ -carbonyl). ^{195}Pt NMR (129 MHz, CDCl_3) $\delta = -3542.5$. $\text{C}_{31}\text{H}_{37}\text{Cl}_2\text{N}_3\text{O}_3\text{PtS}$: calcd. C, 46.68; H, 4.68; N, 5.27; S, 4.02; found: C, 46.58; H, 4.76; N, 5.13; S, 4.06.

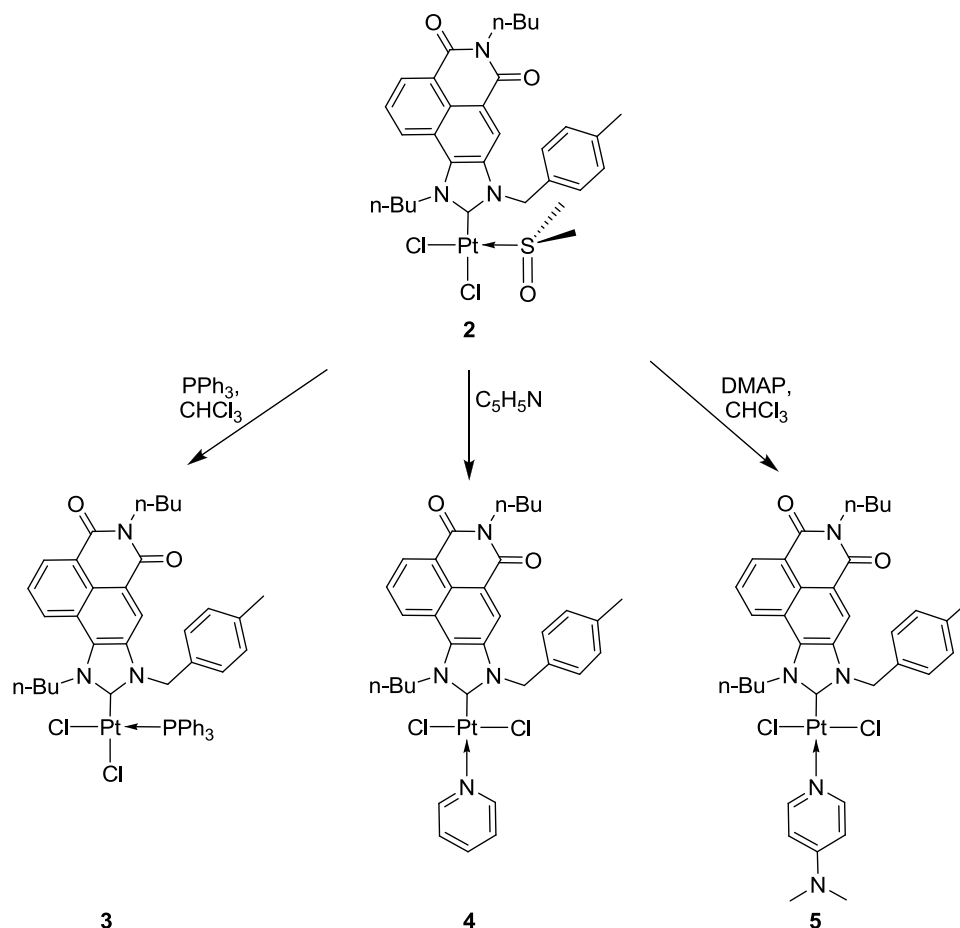
Synthesis of cis-[(NHC)Pt(PPh₃)(Cl)₂], complex 3:

A Schlenk tube was charged with a magnetic stir bar, complex **2** (80 mg, 0.1 mmol), triphenylphosphine (26 mg, 1 mmol) and 2 ml chloroform. The mixture was stirred for 4 hours at 50 °C and after cooling to room temperature, and evaporation of all volatiles, the product was purified by column chromatography, eluting with DCM/ethyl acetate = 5:0.1. Yield: 88 mg (61%) pale yellow solid with m.p. decomposition over 120 °C: ^1H NMR (600 MHz, CDCl_3) $\delta = 0.975$ (t, $J = 7.4$ Hz, 3H, CH_3 -5-*n*-Bu), 1.024 (t, $J = 7.3$ Hz, 3H, CH_3 -10-*n*-Bu), 1.441-1.471 (m, 2H, CH_2CH_3 -5-*n*-Bu), 1.541-1.608 (m, 1H a- CH_2CH_3 -10-*n*-Bu), 1.611-1.651 (m, 1H, b- CH_2CH_3 -10-*n*-Bu), 1.661-1.718 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$ -5-*n*-Bu), 1694-1.751 (m, 1H, a- $\text{CH}_2\text{CH}_2\text{CH}_3$ -10-*n*-Bu), 2.244 (s, 3H, CH_3 -*p*-xylyl), 2.284-2.359 (m, 1H, b- $\text{CH}_2\text{CH}_2\text{CH}_3$ -10-*n*-Bu), 4.091-4.163 (m, 2H, NCH_2 -5-*n*-Bu), 4.674 (d, $J = 14.8$ Hz, 1H, a- NCH_2 -*p*-xylyl), 4.659-4.699 (m, 1H, a- NCH_2 -10-*n*-Bu), 5.37 (m, 1H, b- NCH_2 -10-*n*-Bu), 6.479 (d, $J = 14.8$ Hz, 1H, b- NCH_2 -*p*-xylyl), 7.034 (d, $J = 8.1$ Hz, 2H, **H2,6**-*p*-

xylyl), 7.181-7.221 (m, 6H, *m*-ArH), 7.292-7.322 (m, 3H, *p*-ArH), 7.496 (d, $J = 8.1$ Hz, 2H, **H3,5**-*p*-xylyl), 7.545-7.614 (s, 6H, *o*-ArH), 7.904 (dd, $J = 7.4, 8.5$ Hz, 1H, **H2**-naphthyl), 8.274 (s, 1H, **H7**-naphthyl), 8.326 (dd, $J = 0.7, 8.5$ Hz, 1H, **H1**-naphthyl), 8.662 (dd, $J = 0.7, 7.4$ Hz, 1H, **H3**-naphthyl). ^{13}C NMR (151 MHz, CDCl_3) $\delta = 13.64$ (CH_3 -5-*n*-Bu), 13.79 (CH_3 -10-*n*-Bu), 20.15 (CH_2CH_3 -10-*n*-Bu), 20.37 (CH_2CH_3 -5-*n*-Bu), 21.16 (CH_3 -*p*-xylyl), 30.05 ($\text{CH}_2\text{CH}_2\text{CH}_3$ -5-*n*-Bu), 30.34 ($\text{CH}_2\text{CH}_2\text{CH}_3$ -10-*n*-Bu), 40.65 (NCH_2 -5-*n*-Bu), 51.50 (NCH_2 -10-*n*-Bu), 52.94 (NCH_2 -*p*-xylyl), 116.52 (**C7**-naphthyl), 118.76 (**Ar**- ^{13}C), 123.71 (**Ar**- ^{13}C), 125.44 (**Ar**- ^{13}C), 126.47 (**C1**-naphthyl), 128.15 (**C2**-naphthyl), 128.30 (**Ar**- ^{13}C), 128.34 (d, $^2J_{\text{C-P}} = 11$ Hz, *m*-ArC), 128.42 (**C3,5**-*p*-xylyl), 129.68 (**C2,6**-*p*-xylyl), 130.12 (**Ar**- ^{13}C), 130.35 (**C3**-naphthyl), 131.27 (brs, *p*-ArC), 131.71 (**Ar**- ^{13}C), 133.97 (d, $^2J_{\text{C-P}} = 11$ Hz, *o*-ArC), 138.58 (**Ar**- ^{13}C), 163.18 ($^{13}\text{C}_{\text{C4}}$ -carbonyl), 163.66 ($^{13}\text{C}_{\text{C6}}$ -carbonyl), 164.54 (brs, $^{13}\text{C}_{\text{NHC}}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3) $\delta = 8.63$ (s, PPh_3). ^{195}Pt NMR (129 MHz, CDCl_3) $\delta = -3993$ (d, $^1J_{\text{Pt-P}} = 3813$ Hz). $\text{C}_{47}\text{H}_{46}\text{Cl}_2\text{N}_3\text{O}_2\text{P}$: calcd. C, 57.49; H, 4.72; N, 4.28; found: C, 57.24; H, 5.31; N, 4.19.

Synthesis of trans-[(NHC)Pt(C₅H₅N)(Cl)₂], complex 4:

A Schlenk tube was charged with a magnetic stir bar, complex **2** (100 mg, 0.125 mmol) and pyridine (2 ml). The mixture was stirred for 18 hours at 50 °C and after cooling to room temperature and evaporation of all volatiles, the product was purified by column chromatography, eluting with DCM/ethyl acetate = 5:0.1. Yield: 95 mg (95%) pale yellow solid with m.p. decomposition over 120 °C: ^1H NMR (600 MHz, CDCl_3) $\delta = 0.972$ (t, $J = 7.4$ Hz, 3H, CH_3 -5-*n*-Bu), 1.187 (t, $J = 7.4$ Hz, 3H, CH_3 -10-*n*-Bu), 1.405-1.468 (m, 2H, CH_2CH_3 -5-*n*-Bu), 1.671-1.722 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$ -5-*n*-Bu), 1.763-1.825 (m, 2H, CH_2CH_3 -10-*n*-Bu), 2.253-2.311 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$ -10-*n*-Bu), 2.309 (s, 3H, CH_3 -*p*-xylyl), 4.134-4.159 (m, 2H, NCH_2 -5-*n*-Bu), 5.569-5.597 (m, 2H, NCH_2 -10-*n*-Bu), 6.404 (s, 2H, NCH_2 -*p*-xylyl), 7.176 (d, $J = 8.1$ Hz, 2H, **H3,5**-*p*-xylyl), 7.431-7.455 (m, 2H, **H3,5**-pyr), 7.545 (d, $J = 8.1$ Hz, 2H, **H2,6**-*p*-xylyl), 7.858 (tt, $J = 1.6, 7.6$ Hz, 1H, **H4**-pyr), 7.940 (dd, $J = 7.4, 8.5$ Hz, 1H, **H2**-naphthyl), 8.533 (s, 1H, **H7**-naphthyl), 8.627 (dd, $J = 0.8, 8.5$ Hz, 1H, **H1**-naphthyl), 8.669 (dd, $J = 0.8, 7.4$ Hz, 1H, **H3**-naphthyl), 9.053-9.066 (m, 2H, **H2,6**-pyr). ^{13}C NMR (151 MHz, CDCl_3) $\delta = 13.79$ (CH_3 -5-*n*-Bu), 13.86 (CH_3 -10-*n*-Bu), 20.12



Scheme 2. Synthesis of platinum(II) complexes 3-5.

pyridine as a solvent. However, the application of this straightforward protocol for preparation of complex **1** was inappropriate due to generation of high concentrations of carbene and its fast dimerization to a respective ethylenetetramine. A successful workaround was to use a Pd precursor that already contains the pyridine ligand and use the standard $\text{K}_2\text{CO}_3/\text{THF}$ protocol.

Pt(II) complexes **3-5** were prepared by substitution of the labile DMSO ligand in complex **2** with triphenylphosphine, pyridine or 4-dimethylaminopyridine respectively at 50 °C (Scheme 2). The new complexes were isolated as pale yellow solids, stable under normal conditions in moderate to high yields.

All new complexes were fully characterized by 1D and 2D ^1H and ^{13}C NMR experiments; complexes **2-5** were additionally studied by ^{195}Pt NMR as well. The ^1H NMR spectrum of palladium complex **1** was influenced by the pyridine ligand coordination, resulting in a downfield shift of the signal for the α -pyridine protons by 0.5 ppm, compared to the same signal of the free pyridine. The carbene atom in complex **1** resonates at 167 ppm in the ^{13}C NMR. The equivalence of the

benzylic CH_2 -protons as consequence of presence of mirror plane confirms *trans*-configuration of complex **1**. In the ^1H NMR spectrum of complex **2**, two singlets are observed for the methyl groups of the DMSO ligand at 2.98 and 3.54 ppm respectively, the coordination of DMSO ligand is additionally confirmed by presence of platinum satellites in ^1H spectrum at 250 MHz for the methyl groups due to $^3\text{J}_{\text{H-Pt}}$ coupling constant, which are missing in the ^1H spectrum at 600 MHz due to chemical shift anisotropy (CSA) relaxation (Fig. 1). As magnetic field increases, CSA contribution shortens the ^{195}Pt relaxation times, which broadens the linewidths of platinum satellites. The latter observation and the splitting of the diastereotopic benzylic protons into a doublets support the *cis*-configuration of the complex **2** due to the absence of a mirror plane. The carbene carbon of complex **2** resonates at 158 ppm; the absence of Pt satellites is likely due to low intensity of the signal and CSA effects at high magnetic field, while the ^{195}Pt signal of complex **2** appears at -3543 ppm, a value which is more inherent to the ^{195}Pt chemical shifts of saturated imidazolin-2-ylidene NHC system [41],

which as a “softer” ligand, is a stronger σ -donor causing upfield shift of the ^{195}Pt resonance [42].

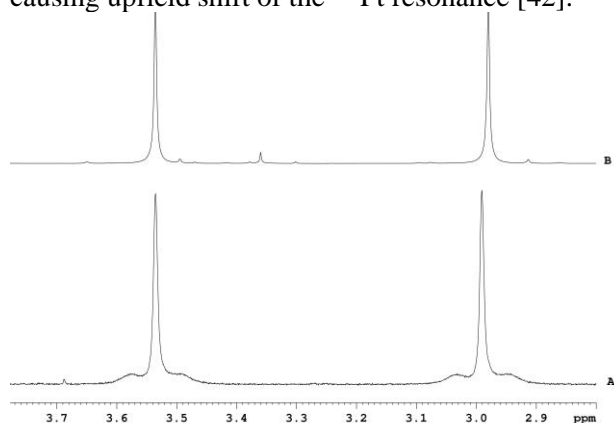


Fig. 1. Expansion of region of DMSO ligand methyl groups in ^1H NMR spectrum of complex **2**. **A:** measured at 250 MHz and showing satellites with $^3J_{\text{H-Pt}}$ coupling; **B:** the same spectrum measured at 600 MHz, in which these satellites are missing due to CSA.

Similarly to complex **2**, platinum complex **3** demonstrates absence of mirror plane as well, as a result of its *cis*-configuration consequently every diastereotopic CH_2 -group shows a pair of distinct signals in the ^1H NMR spectrum. The carbene atom in complex **3** resonates at 164 ppm in the ^{13}C NMR spectrum. The PPh_3 ligand's $^3\text{P}\{^1\text{H}\}$ signal is observed as a singlet at 8.6 ppm with platinum satellites due to $^1J_{\text{P-Pt}}$ coupling constant of 3813 Hz. This value supports the *cis*-configuration of the complex - commonly, values over 3000 Hz are a typical spectral characteristic of *cis*-complexes [43]. The ^{195}Pt signal resonates as a doublet at -3993 ppm and the substitution of the DMSO ligand with a “softer” ligand as PPh_3 shifts the resonance downfield with 450 ppm.

The ^1H -NMR spectrum of **P1** consists of four groups of signals (Fig. 1). The aromatic protons of 7-nitrobenzofurazane (NBD) moieties close to the ring nitrogen atoms and the CH_2 protons adjacent to ring nitrogens appear at 6.53 ppm and between 2.83-2.94 ppm, respectively, while the signals of $\text{C-CH}_2\text{-C}$ protons are around 1.76 ppm.

The ^1H NMR spectra of platinum complexes **4** and **5** demonstrate symmetry of both molecules due to presence of mirror plane, confirming the *trans*-configuration of the complexes. The ^1H NMR spectrum of platinum complexes **4** reveals the same tendency as his palladium analogue for the signal of α -pyridine protons, which is shifted upfield with 0.5 ppm in comparison with the same signal of the free pyridine. The ^{13}C signal for the carbene carbon in complex **4** is observed at 156 ppm, which is

upfield shifted with 11 ppm in comparison with the palladium analogue as result of the more electron-rich properties of platinum and its greater π -backbonding contribution in the carbene-metal bond [31, 44, 45]. The ^{195}Pt chemical shifts of complexes **4** and **5** are observed correspondingly at -2965 and -2957 ppm (Fig. 2).

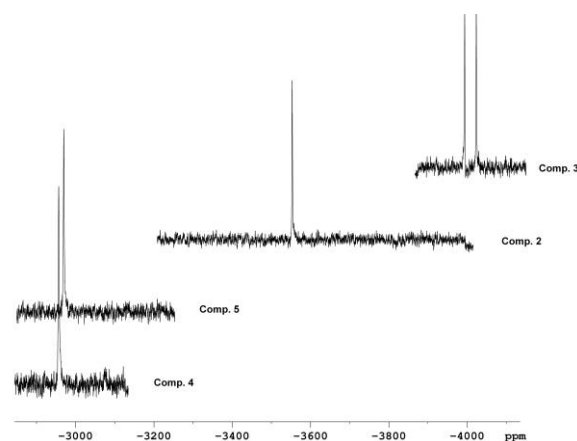


Fig. 2. ^{195}Pt NMR spectra of complexes **2-5**.

DFT study of complexes 1-5

Calculated thermodynamic parameters of complexes **1-5** at standard conditions are compared in Table 1. Calculated relative enthalpy values for *cis* and *trans* configuration at B3LYP/ECP (LanL2DZ for Pd and 6-31G* for other atoms) level including SMD exhibit correct tendency for all investigated complexes **1-5** (Table 1) and are in agreement with the experimentally obtained configuration of complexes which is denoted in Table 1 in bold. The differences in entropy are small and influence insignificantly the position of final thermodynamic equilibrium. The final ΔG° values accumulate computational errors both in enthalpy and in entropy, but the population distributions were predicted very well for all complexes **1-5** at relative low level of theory. From the fact that the obtained configurations of studied complexes are thermodynamically more stable, the conclusion that the studied ligand exchange reaction is carried out under thermodynamic control can be made.

CONCLUSION

Four platinum and one palladium PEPPSI type functionalized new N-heterocyclic carbene complexes were easily synthesized by ligand exchange reaction. The comparison of the ^{13}C NMR carbene resonances of palladium pyridine complex


Table 1. Thermodynamic parameters of *cis* and *trans* configurations of complexes at 298 K. Experimentally determined configurations are denoted in bold.^a

Complex (solvent)	Configuration	ΔH° (kcal mol ⁻¹)	ΔS° (cal K ⁻¹ mol ⁻¹)	ΔG° (kcal mol ⁻¹)	Population (%)
1 (THF)	<i>trans</i>	0.00	0.00	0.00	99.97
	<i>cis</i>	4.88	0.18	4.82	0.03
2 (THF)	<i>trans</i>	2.72	-0.08	2.74	0.97
	<i>cis</i>	0.00	0.00	0.00	99.03
3 (CDCl ₃)	<i>trans</i>	4.49	1.77	3.96	0.12
	<i>cis</i>	0.00	0.00	0.00	99.88
4 (Pyridine)	<i>trans</i>	0.00	0.00	0.00	99.60
	<i>cis</i>	2.61	-2.23	3.27	0.40
5 (CDCl ₃)	<i>trans</i>	0.00	0.00	0.00	99.93
	<i>cis</i>	3.77	-1.79	4.30	0.07

^a Calculated at B3LYP/ECP (LanL2DZ for Pd and 6-31G* for other atoms) level of theory including SMD.

1 and platinum pyridine complex **4** demonstrates the importance of metal center on π -backbonding contribution to the metal-carbene bond. The configuration of all complexes was determined by NMR spectroscopy. The DFT calculated thermodynamic parameters are in agreement with observed stereochemistry of all complexes, which means that the studied ligand exchange reaction is carried out under thermodynamic control.

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Electronic Supplementary Data available here. 

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НАФТАЛИМИД-БАЗИРАНИ ПЛАТИНОВИ(II) И ПАЛАДИЕВИ(II) N-ХЕТЕРОЦИКЛЕНИ КАРБЕНОВИ КОМПЛЕКСИ: СИНТЕЗ И ДОКАЗВАНЕ НА СТРУКТУРАТА

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(Резюме)

Представен е синтез и охарактеризирането на пет каталитично приложими Pd(II) и Pt(II) комплекси включващи N-хетероциклени карбени (NHCs) получени от заместени 1,8-нафталимиди и σ -донорни неутрални монодентатни лиганди (DMSO, PPh₃, C₆H₅N и 4-диметиламинопиридин (DMAPI)). Структурата и конфигурацията на комплексите е доказана на базата на комбинация от ЯМР и DFT изследвания.