Naphthalimide-based platinum(II) and palladium(II) N-heterocyclic carbone 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-type (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 hydroislylation 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 carbone 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[e]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)2Cl2] [29], trans-[Pd(Pyr)2Cl2] [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, 39.53 MHz for 31P NMR), and coupling constants were determined from the 2D NMR spectra. HRMS analyses were obtained on a Bruker microTOF-Q II.
242.92 MHz for $^{31}$P NMR and 129.01 MHz for $^{195}$Pt NMR), spectrometer with TMS (85% $\text{H}_2\text{PO}_4$ for $^{31}$P) as internal standard for proton and carbon chemical shifts ($\delta$, ppm). $^{195}$Pt NMR spectra are referred to the signal of 1.2M Na$_2$PtCl$_6$ in D$_2$O. $^1$H 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 $^1$H 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 mm). Elemental analyses were performed by Microanalytical Service Laboratory of Faculty of Chemistry and Pharmacy, University of Sofia, using Vario EL 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.ghcm.bas.bg) using program package GAUSSIAN 09 [32]. Geometry optimizations were performed by using density functional theory [33–35] with B3LYP functionals [36, 37]. For the as 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 cis-[(NHC)Pd(Pyr)(Cl)]$_2$, complex 1:**

A Schlenk tube was charged with a magnetic stir bar, $\text{NHC.HCl}$ (250 mg, 0.51 mmol), cis-[(DMSO)$_2$(Cl)$_2$] (240 mg, 1.1 equiv.), 2 ml dry THF and finely powdered freshly dried K$_2$CO$_3$ (140 mg, 2 equiv.). 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. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ = 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$_2$CH$_2$-5-n-Bu), 1.660-1.717 (m, 2H, CH$_2$CH$_2$-5-n-Bu), 1.792-1.854 (m, 2H, CH$_2$CH$_2$-10-n-Bu), 2.318 (s, 3H, CH$_3$-p-xyllyl), 2.301-2.361 (m, 2H, CH$_2$CH$_2$-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-xyllyl), 7.189 (d, $J$ = 8.0 Hz, 2H, H$_3$-p-xyllyl), 7.402-7.425 (2H, H$_3$-p-xyllyl), 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$_2$-pyr).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ = 13.84 (CH$_3$-5-n-Bu), 13.92 (CH$_3$-10-n-Bu), 20.25 (CH$_2$CH$_2$-5-n-Bu), 20.40 (CH$_2$CH$_2$-10-n-Bu), 21.24 (CH$_2$-p-xyllyl), 30.10 (CH$_2$CH$_2$-5-n-Bu), 40.66 (NCH$_2$-5-n-Bu), 51.60 (NCH$_2$-10-n-Bu), 53.47 (NCH$_2$-p-xyllyl), 116.62 (C7-naphthyl), 119.02 (Ar-C), 123.74 (Ar-C), 124.68 (Ar-C), 124.71 (C3,5-pyr), 125.63 (Ar-C), 126.74 (C1-naphthyl), 127.91 (C2,6-p-xyllyl), 128.18 (C2-naphthyl), 129.88 (C3,5-p-xyllyl), 130.17 (C3-naphthyl), 131.33 (Ar-C), 132.44 (Ar-C), 132.54 (Ar-C), 138.39 (C4-pyr), 138.44 (Ar-C), 151.32 (C2,6-pyr), 163.30 (C6-carbonyl), 163.82 (C4-carbonyl), 166.85 (C$_{\text{NHC}}$).

C$_{16}$H$_{30}$Cl$_2$N$_2$O$_2$Pd: calc. C, 57.52; H, 5.11; N, 7.89; found: C, 57.60; H, 5.12; N, 7.63.

**Synthesis of trans-[(NHC)Pd(Pyr)(Cl)]$_2$, complex 2:**

A Schlenk tube was charged with a magnetic stir bar, $\text{NHC.HCl}$ (250 mg, 0.51 mmol), cis-[(DMSO)$_2$(Cl)$_2$] (240 mg, 1.1 equiv.), 2 ml dry THF and finely powdered freshly dried K$_2$CO$_3$ (140 mg, 2 equiv.). 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: $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ = 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$_2$CH$_2$-5-n-Bu), 1.652-1.701 (m, 2H, CH$_2$CH$_2$-5-n-Bu), 1.731-1.791 (m, 2H, CH$_2$CH$_2$-10-n-Bu), 2.045-2.131 (m, 1H, a-CH$_2$CH$_2$-5-n-Bu), 2.267-2.347 (m, 1H, b-
CH₂(CH₃CH₂-10-n-Bu), 2.305 (s, 3H, CH₃-p-xylyl), 2.981 (s, 3H, CH₃DMSO), 3.537 (s, 3H, CH₃DMSO), 4.132-4.157 (m, 2H, NCH₂-5-n-Bu), 5.221-5.272 (m, 1H, a-NCH₂-10-n-Bu), 5.333-5.381 (m, 1H, b-NCH₂-10-n-Bu), 5.933 (d, J = 16.3 Hz, 1H, a-NCH₂-p-xylyl), 6.478 (d, J = 16.3 Hz, 1H, b-NCH₂-p-xylyl), 7.152 (d, J = 8.2 Hz, 2H, H₂6,6-p-xylyl), 7.212 (d, J = 8.2 Hz, 2H, H₃,3-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, H₁1-naphthyl), 8.707 (dd, J = 0.7, 7.4 Hz, 1H, H₃-naphthyl).¹C NMR (151 MHz, CDCl₃) δ = 13.75 (CH₃-5-n-Bu), 13.83 (CH₃-10-n-Bu), 20.17 (CH₂CH₃-10-n-Bu), 20.28 (CH₂CH₃-5-n-Bu), 21.08 (CH₂-p-xylyl), 30.01 (CH₂CH₂CH₃-5-n-Bu), 30.73 (CH₃CH₂CH₃-10-n-Bu), 40.58 (NCH₂-5-n-Bu), 45.21 (CH₂-DMSO), 45.86 (CHD₂-DMSO), 51.67 (NCH₂-10-n-Bu), 52.06 (NCH₂-p-xylyl), 116.57 (C₇-naphthyl), 119.41 (Ar⁻C), 120.00 (Ar⁻C), 123.83 (Ar⁻C), 126.01 (Ar⁻C), 126.70 (C₁-naphthyl), 126.89 (C₃,5-p-xylyl), 128.41 (C₁-naphthyl), 129.87 (C₂,6-p-xylyl), 130.29 (C₃-naphthyl), 131.11 (Ar⁻C), 131.26 (Ar⁻C), 132.24 (Ar⁻C), 138.40 (Ar⁻C), 158.16 (C₆Naph), 163.05 (C₄-carbonyl), 163.60 (C₆-carbonyl).¹⁹Pt NMR (129 MHz, CDCl₃) δ = -3542.5. C₃H₂Cl₂N₂O₅PtS: 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, 0.125 mmol) and 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, CDCl₃) δ = 0.975 (t, J = 7.4 Hz, 3H, CH₃-5-n-Bu), 1.024 (t, J = 7.3 Hz, 3H, CH₃-10-n-Bu), 1.441-1.471 (m, 2H, CH₂CH₃-5-n-Bu), 1.541-1.608 (m, 1H a-CH₃CH₂-10-n-Bu), 1.611-1.651 (m, 1H, b-CH₃CH₂-10-n-Bu), 1.661-1.718 (m, 2H, CH₂CH₂CH₂-5-n-Bu), 1694-1751 (m, 1H, a-CH₂CH₂CH₂-10-n-Bu), 2.244 (s, 3H, CH₃-p-xylyl), 2.284-2.359 (m, 1H, b-CH₂CH₂CH₂-10-n-Bu), 4.091-4.163 (m, 2H, NCH₂-5-n-Bu), 4.674 (d, J = 14.8 Hz, 1H, a-NCH₂-p-xylyl), 4.659-4.699 (m, 1H, a-NCH₂-10-n-Bu), 5.37 (m, 1H, b-NCH₂-10-n-Bu), 6.479 (d, J = 14.8 Hz, 1H, b-NCH₂-p-xylyl), 7.034 (d, J = 8.1 Hz, 2H, H₂6,6-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, H₁1-naphthyl), 8.662 (dd, J = 0.7, 7.4 Hz, 1H, H₃-naphthyl).¹³C NMR (151 MHz, CDCl₃) δ = 13.64 (CH₃-5-n-Bu), 13.79 (CH₃-10-n-Bu), 20.15 (CH₂CH₃-10-n-Bu), 20.37 (CH₂CH₃-5-n-Bu), 21.16 (CH₂-p-xylyl), 30.05 (CH₂CH₂CH₃-5-n-Bu), 30.34 (CH₂CH₂CH₃-10-n-Bu), 40.65 (NCH₂-5-n-Bu), 51.50 (NCH₂-10-n-Bu), 52.94 (NCH₂-p-xylyl), 116.52 (C₇-naphthyl), 118.76 (Ar⁻C), 123.71 (Ar⁻C), 125.44 (Ar⁻C), 126.47 (C₁-naphthyl), 128.15 (C₂-naphthyl), 128.30 (Ar⁻C), 128.34 (d, J = 11 Hz, m-ArC), 128.42 (C₃,5-p-xylyl), 129.68 (C₂,6-p-xylyl), 130.12 (Ar⁻C), 130.35 (C₃-naphthyl), 131.27 (brs, p-ArC), 131.71 (Ar⁻C), 133.97 (d, J = 11 Hz, o-ArC), 133.58 (Ar⁻C), 163.18 (C₄-carbonyl), 163.66 (C₆-carbonyl), 164.54 (brs, C₆Naph).³¹P[¹H] NMR (243 MHz, CDCl₃) δ = 8.63 (s, PPh₃).³⁹Pt NMR (129 MHz, CDCl₃) δ = -3993 (d, J = 3.5 Hz, 1H, H₃,5-p-xylyl), 4.134-4.159 (m, 2H, NCH₂-5-n-Bu), 5.569-5.597 (m, 2H, NCH₂-10-n-Bu), 6.404 (s, 2H, NCH₂-10-n-Bu), 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, H₂6,6-p-xylyl), 7.838 (tt, J = 7.4, 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, H₁1-naphthyl), 8.669 (dd, J = 0.8, 7.4 Hz, 1H, H₃-naphthyl), 9.053-9.066 (m, 2H, H₂6,6-pyr).¹³C NMR (151 MHz, CDCl₃) δ = 13.79 (CH₃-5-n-Bu), 13.86 (CH₃-10-n-Bu), 20.12
(CH$_2$CH$_2$-5-n-Bu), 20.35 (CH$_3$CH$_2$-10-n-Bu), 21.16 (CH$_3$-p-xyl), 30.05 (CH$_3$CH$_2$CH$_2$-5-n-Bu), 31.13 (CH$_3$CH$_2$CH$_2$-10-n-Bu), 40.56 (NCH$_2$-5-n-Bu), 50.92 (NCH$_2$-10-n-Bu), 52.65 (NCH$_2$-p-xyl), 116.67 (C7-naphthyl), 118.74 (Ar$_{-}$C$_{1}$), 119.03 (Ar$_{-}$C$_{3}$), 123.63 (Ar$_{-}$C$_{4}$), 125.03 (C$_{3}$,5-pyr), 125.63 (Ar$_{-}$C$_{4}$), 126.82 (C1-naphthyl), 127.59 (C$_{2}$,6-p-xyl), 127.91 (C2-naphthyl), 129.74 (C$_{3}$,5-p-xyl), 129.96 (C3-naphthyl), 131.67 (Ar$_{-}$C$_{4}$), 132.04 (Ar$_{-}$C$_{2}$), 132.05 (Ar$_{-}$C$_{5}$), 132.14 (Ar$_{-}$C$_{1}$), 132.29 (C4-pyr), 151.35 (C$_{2}$,6-p-xyl), 155.91 (C$_{3}$NHC), 163.29 (C$_{6}$-carbonyl), 163.83 (C$_{4}$-carbonyl). $^{195}$Pt NMR (129 MHz, CDCl$_3$) $\delta$ = -2965 (s). C$_{34}$H$_{30}$Cl$_2$N$_2$O$_5$Pt: calc'd. C, 51.13; H, 4.54; N, 7.02; found: C, 51.33; H, 4.44; N, 7.19.

**Synthesis of trans-[(NHC)Pt(DMAP)](Cl)$_2$, complex 5:**

A Schlenk tube was charged with a magnetic stir bar, complex 2 (80 mg, 0.1 mmol), 4-dimethylaminopyridine (15 mg, 1.1 eqv.) and 2 ml chloroform. The mixture was stirred for 18 hours at 50 °C and after cooling to room temperature and evaporation of all volatiles, the product was obtained. By reaction of NHC precursors, palladium complex 2 were synthetized via in situ generation of the carbene, by deprotonating the imidazolium salt (NHC.HCl) with the mild base K$_2$CO$_3$, in presence of appropriate organometallic precursor in dry THF (Scheme 1), following our previous reported method [31, 40]. The precursor is trans-[Pd(Pyr)$_2$(Cl)$_2$] in case of complex 1 and respectively cis-[Pt(DMSO)$_2$(Cl)$_2$] in case of complex 2. N-heterocyclic carbene complexes of type 1, known as PEPSI type could in theory be obtained [18] by reaction of NHC precursors, palladium dichloride, and potassium carbonate in

Scheme 1. Synthesis of complexes 1 and 2.

**RESULTS AND DISCUSSION**

**Synthesis and characterization**

Palladium complex 1 and platinum complex 2 were synthetized via in situ generation of the carbene, by deprotonating the imidazolium salt (NHC.HCl) with the mild base K$_2$CO$_3$, in presence of appropriate organometallic precursor in dry THF (Scheme 1), following our previous reported method [31, 40]. The precursor is trans-[Pd(Pyr)$_2$(Cl)$_2$] in case of complex 1 and respectively cis-[Pt(DMSO)$_2$(Cl)$_2$] in case of complex 2. N-heterocyclic carbene complexes of type 1, known as PEPSI type could in theory be obtained [18] by reaction of NHC precursors, palladium dichloride, and potassium carbonate in
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 K$_2$CO$_3$/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 $^1$H and $^{13}$C NMR experiments; complexes 2–5 were additionally studied by $^{195}$Pt NMR as well. The $^1$H NMR spectrum of palladium complex 1 was influenced by the pyridine ligand coordination, resulting in a downfield shift of the signal for the $\alpha$-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 $^1$H 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 $^1$H spectrum at 250 MHz for the methyl groups due to $^3$J$_{H_{	ext{Pt}}}$ coupling constant, which are missing in the $^1$H 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].

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 $^1$H NMR spectrum. The carbene atom in complex 3 resonates at 164 ppm in the $^{13}$C NMR spectrum. The PPh$_3$ ligand’s $^{31}$P($^1$H) signal is observed as a singlet at 8.6 ppm with platinum satellites due to $^1$J$_{P\cdots Pt}$ 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 $^1$H-NMR spectrum of P1 consists of four groups of signals (Fig. 1). The aromatic protons of 7-nitrobezofurazane (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 C-CH$_2$-C protons are around 1.76 ppm.

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

**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 $\Delta G^\circ$ 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

<table>
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<th>Complex (solvent)</th>
<th>Configuration</th>
<th>ΔH° (kcal mol⁻¹)</th>
<th>ΔS° (cal K⁻¹ mol⁻¹)</th>
<th>ΔG° (kcal mol⁻¹)</th>
<th>Population (%)</th>
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<td>2 (THF)</td>
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<td>0.00</td>
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<td>3 (CDCl₃)</td>
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<td>1.77</td>
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<tr>
<td>4 (Pyridine)</td>
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</table>

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.

REFERENCES


НАФТАЛИМИД-БАЗИРИANI ПЛАТИНОВИ(II) И ПАЛАДИЕВИ(II) N-ХЕТЕРОЦИКЛЕНI КАРБЕНОВИ КОМПЛЕКСИ: СИНТЕЗ И ДОКАЗАВАНЕ НА СТРУКТУРАТА

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(Резюме)

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