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Structural and spectroscopic studies of Au(III) and Pd(II) chloride complexes and organometallics with 2-benzylpyridine

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HIGHLIGHTS

- Au(III)/Pd(II) complexes/organometallics with 2-benzylpyridine were studied by NMR.
- Nitrogen metallation in 2-benzylpyridine results in ^{15}N shielding and ^{1}H deshielding.
- 2bzpyH^{+} [AuCl$_4$]$^{-}$ ionic pair was studied by single crystal X-ray diffraction.

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ABSTRACT

Au(III) and Pd(II) chloride complexes with 2-benzylpyridine (2bzpy) – [Au(2bzpy)Cl$_3$] and *trans*-[Pd(2bzpy)$_2$Cl$_2$], as well as Au(III) chloride organometallics with monoanionic form of 2bzpy, deprotonated in the benzyl side group at the *ortho*-carbon C(2′) (2bzpy*) – [Au(2bzpy*)Cl$_2$], were studied by ^{1}H, ^{13}C and ^{15}N NMR. ^{1}H, ^{13}C and ^{15}N coordination shifts (i.e. differences of chemical shifts for the same atom in the complex and ligand molecules) were discussed in relation to the molecular structures and the coordination modes, as well as to the factors influencing nuclear shielding. Analogous NMR measurements were performed for the new (2bzpyH)[AuCl$_4$] salt, studied also by single crystal X-ray diffraction.

1. Introduction

2-Benzylpyridine (2bzpy), being an analogue of 2-phenylpyridine (2ppy) (Scheme 1), is an azine ligand, which is known to coordinate transition metal ions, such as Au(III) and Pd(II), in two alternative ways: as a monodentate N(1)-donor or a N(1),C(2′)-chelating agent 2bzpy* (2bzpy* = monoanionic form of 2bzpy, deprotonated in the benzyl side group at the *ortho*-carbon C(2′)). The former complexation mode occurs in [Au(2bzpy)Cl$_3$] [1] and *trans*-[Pd(2bzpy)$_2$Cl$_2$] [2,3], while the latter in [Au(2bzpy*)Cl$_2$] [1,4] (Scheme 2).

These compounds are of increasing interest due to their catalytic properties (*trans*-[Pd(2bzpy)$_2$Cl$_2$] in hydrogenation of unsaturated functional groups [5], [Au(2bzpy*)Cl$_2$] in introduction of amine and alkyne substituents into oligosaccharides [6]) and cytotoxicity ([Au(2bzpy*)Cl$_2$] is active against cancer [7] and parasites [8]). [Au(2bzpy*)Cl$_2$] and its [Au(2-(1,1-dimethylbenzyl)pyridine*)Cl$_2$] analogue are also widely used as precursors for preparation of some other compounds with antitumour, antibacterial, antifungal or antiviral properties [9–17]. However, they still remain insufficiently characterized, as only their IR and ^{1}H (but not ^{13}C and ^{15}N) NMR spectra were published [1–4]. In contrast to Au(III) and Pd(II) chloride complexes and organometallics with 2ppy, for which two single crystal X-ray structures were reported ([Au(2ppy)Cl$_3$] – YIDMAA [18], [Au(2ppy*)Cl$_2$] – IJAQEP [19]; all refcodes derive from the Cambridge Structural Database [20]), for the studied 2bzpy analogues such data are unavailable. Recently, we have reported the ^{1}H, ^{13}C and ^{15}N NMR spectra for [Au(2ppy)Cl$_3$], *trans*- and *cis*-[Pd(2ppy)$_2$Cl$_2$] [21], and [Au(2ppy*)Cl$_2$] [22], assigning all signals by ^{1}H–^{13}C and ^{1}H–^{15}N HMQC and HMBC methods. In this paper we have applied the same techniques for [Au(2bzpy)Cl$_3$], *trans*-[Pd(2bzpy)$_2$Cl$_2$] and [Au(2bzpy*)Cl$_2$]. Additionally, we describe the results of analogous NMR measurements and single crystal X-ray diffraction for the new (2bzpyH)[AuCl$_4$] salt.

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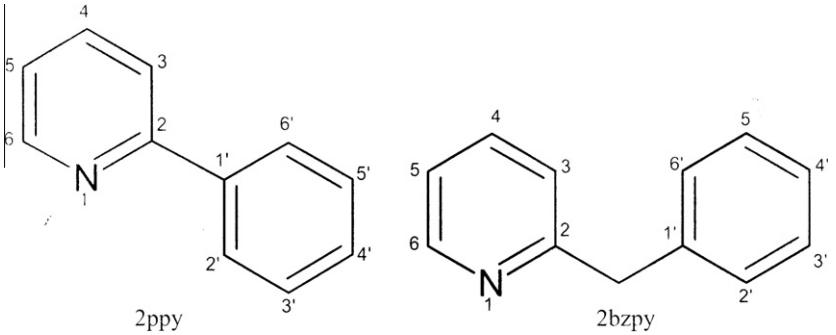


Scheme 1. 2-Phenylpyridine (2ppy) and 2-benzylpyridine (2bzpy), with the numbering scheme.

2. Experimental

2.1. Materials

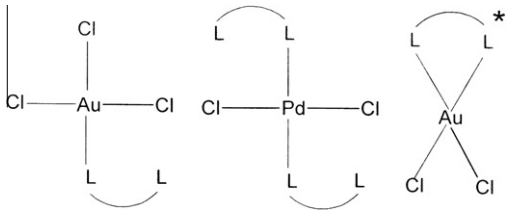
2bzpy (98% purity) was purchased from Aldrich; Au (99.99%) from Polish Mint, $PdCl_2$ (99.9%) from POCh Gliwice (Poland). Aqueous $HAuCl_4$ solution (*ca.* 0.05 M) was prepared by dissolving Au in *aqua regia* followed by the removal of HNO_3 and HCl excess by boiling. Solid $NaAuCl_4$ and K_2PdCl_4 were prepared in water by the reactions of $HAuCl_4$ with NaOH and $PdCl_2$ with KCl, respectively, and evaporation to dryness.

2.2. Syntheses and identification by far-IR and ^1H NMR

The (2bzpyH)[$AuCl_4$] salt, although simple, is new. It was obtained by stirring aqueous $HAuCl_4$ solution with 2bzpy in ethanol (1:1; 5 h, 20 °C). After concentration, the overnight-formed precipitate was washed with ethanol and diethyl ether, giving yellow crystals suitable for X-ray structural analysis (yield *ca.* 90%); elemental analysis: C 28.3%, H 2.7%, N 2.8% (calculated for $AuC_{12}H_{12}NCl_4$: C 28.3%, H 2.4%, N 2.8%). The far-IR spectrum (measured in polyethylene by a Perkin–Elmer Spectrum 2000 FT-IR spectrometer with a triglycerin sulphate detector) exhibited the characteristic ν_{AuCl} stretching mode at 352 cm^{-1}, consistent with the literature data for free $[AuCl_4]^-$ anions (350 cm^{-1} [23]).

The [Au(2bzpy)Cl_3] and *trans*-[Pd(2bzpy)$_2Cl_2$] complexes, as well as the [Au(2bzpy*)Cl_2] organometallic are known. Both Au(III) compounds were synthesized by the method of Cinellu et al. [1], i.e. by stirring $NaAuCl_4$ in water with 2bzpy in ethanol (1:1) for 1 h at 20 °C or for 5 h at 80 °C, respectively, while the Pd(II) species by the method of Hiraki et al. [2], i.e. by stirring K_2PdCl_4 in water with 2bzpy in ethanol (1:2) for 3 h at 20 °C. Their composition was confirmed by elemental analysis: [Au(2bzpy)Cl_3]: C 30.2%, H 2.4%, N 3.4% (calculated for $AuC_{12}H_{11}NCl_3$: C 30.5%, H 2.3%, N 3.0%); *trans*-[Pd(2bzpy)$_2Cl_2$]: C 56.0%, H 4.6%, N 5.6% (calculated for $PdC_{24}H_{22}N_2Cl_2$: C 55.9%, H 4.3%, N 5.4%); [Au(2bzpy*)Cl_2]: C 32.6%, H 2.5%, N 3.4% (calculated for $AuC_{12}H_{10}NCl_2$: C 33.1%, H 2.3%, N 3.2%).

The far-IR spectra revealed the following ν_{AuCl} or ν_{PdCl} stretching vibrations: [Au(2bzpy)Cl_3]: 360 cm^{-1} (Cinellu et al.: 362 cm^{-1} [1]) – a broad band, being probably an overlap of three ν_{AuCl} modes ($2A_1 + B_1$) predicted by group theory for MXY_3 square-planar molecules with C_{2v} symmetry [23]; *trans*-[Pd(2bzpy)$_2Cl_2$]: 340 and 336 cm^{-1} (Hiraki et al.: 352 and 344 cm^{-1} [2]) – two maxima, deriving, most likely, from both rotational isomers discovered by Hiraki et al. [2], each giving one ν_{PdCl} mode (B_{2u}) predicted for *trans*-MX_2Y_2 square-planar molecules with D_{2h} symmetry [23]; [Au(2bzpy*)Cl_2]: 355 and 348 cm^{-1} (Cinellu et al.: 358 cm^{-1} [1]) – two ν_{AuCl} modes ($A_1 + B_2$) predicted for $M(XX)Y_2$ square-planar molecules of *cis*-geometry with C_{2v} symmetry [23].



Scheme 2. [Au(LL)Cl_3] and *trans*-[Pd(LL)$_2Cl_2$] complexes with N(1)-monodentately bonded neutral LL molecules and [Au(LL*)Cl_2] organometallics with N(1), C(2*)-chelated LL* monoanionic ligands (LL = various 2-arylpyridines, *e.g.* 2ppy, 2bzpy).

The ^1H NMR spectra are nearly identical with those published for [Au(2bzpy)Cl_3] by Cinellu et al. [1], *trans*-[Pd(2bzpy)$_2Cl_2$] by Hiraki et al. [2], and [Au(2bzpy*)Cl_2] by Cinellu et al. and Shaw et al. [1,4], which confirms the identity of these compounds; their detailed data are described in the further part of this paper.

2.3. NMR measurements

^1H–^{13}C and ^1H–^{15}N two-dimensional NMR spectra were measured at 303 K in $CDCl_3$, CD_2Cl_2, CD_3CN or DMSO-d_6, by a Bruker Avance III 700 MHz NMR spectrometer. The ^1H–^{13}C HMQC, ^1H–^{13}C HMBC and ^1H–^{15}N HMBC experiments were adjusted for $^1J_{H-C}$ = 150 Hz, $^nJ_{H-C}$ = 10 Hz, $^nJ_{H-N}$ = 5 Hz, with the following parameters: $\pi/2$ pulse lengths for ^1H: 9–10 μs, ^{13}C: 12–13 μs, ^{15}N: 23–24 μs; acquisition time for ^1H–^{13}C HMQC and HMBC: 0.2–0.3 s, for ^1H–^{15}N HMBC: 0.07–0.08 s; relaxation delay for ^1H–^{13}C HMQC and HMBC: 1.5 s, for ^1H–^{15}N HMBC: 2 s. As references were used: TMS for ^1H and ^{13}C (with residual ^1H and ^{13}C solvent signals as primary references – in $CDCl_3$: 7.24 ppm and 77.2 ppm, in CD_2Cl_2: 5.32 ppm and 54.0 ppm, in CD_3CN: 1.94 ppm and 1.4 ppm, in DMSO-d_6: 2.50 ppm and 39.5 ppm); neat nitromethane for ^{15}N.

2.4. X-ray diffraction studies

X-ray data for the single crystal of (2bzpyH)[$AuCl_4$], obtained directly from the synthesis by slow evaporation of the ethanol–water solvent, was collected with an Oxford Sapphire CCD diffractometer, using MoKα radiation, by ω–2θ method with numerical absorption correction [24]; further experimental details are listed in Table 1. The structure was solved with direct methods and refined with the full-matrix least-squares method on F^2 using SHELX-97 [25] and PLATON [26], without extinction correction. Hydrogen atoms were located from the difference maps and constrained. The space group was determined basing on the systematic absences. The respective CIF file is available at Cambridge Crystallographic Data Centre with deposition number CCDC 873251.

Table 1
Crystal structure data and X-ray experimental details for (2bzpyH)[$AuCl_4$].

Compound	(2bzpyH)[$AuCl_4$]
Empirical formula	$C_{12}H_{12}AuCl_4N$
Molecular weight	508.99
Crystal system	Orthorhombic
Space group	Pbca
a (Å)	7.4262(3)
b (Å)	15.8385(7)
c (Å)	25.3806(11)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	2985.3(2)
Z	8
Density (Mg/m^3)	2.265
μ (mm^{-1})	10.552
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal size (mm)	0.48 × 0.30 × 0.06
Max. and min. transmission	0.5890 and 0.0799
θ Range	2.57–28.44
Reflections collected/unique/Rint	18972/3526/0.0472
Final R1/wR2 indices [$I > 2\sigma(I)$]	0.0305/0.0738
Final R1/wR2 indices all data	0.0500/0.0799
Goodness of fit	0.966
Residual density peaks (e Å^{-3})	1.308/−0.910

3. Results and discussion

3.1. Crystal and molecular structure of 2-benzylpyridinium tetrachloraurate(III)

The perspective view of the (2bzpyH)[$AuCl_4$] salt is presented at Fig. 1, its packing in the crystal lattice – at Fig. 2. The crystal structure data are collected in Table 1, the bond lengths and angles within the 2bzpyH$^+$ cation – in Table 2.

The symmetry of (2bzpyH)[$AuCl_4$] (orthorhombic, Pbca) is higher than for (2bzpyH)$_4$[Sb_2Cl_{10}] (LUHVOZ; Triclinic, $P\bar{1}$ [27]). The geometry of pyridine and phenyl rings is similar for both salts, as their bond lengths and angles are nearly the same; in contrast, their orientation is different: in (2bzpyH)[$AuCl_4$] the dihedral angle between both rings is uniform for all molecules (57.7°; it results from the N(1)–C(2)–C(7)–C(1′), C(3)–C(2)–C(7)–C(1′), C(2)–C(7)–C(1′)–C(2′), C(2)–C(7)–C(1′)–C(6′) torsion angles of 37.2(8)°, 34.1(6)°, 32.6(8)°, and 28.2(5)°), while in (2bzpyH)$_4$[Sb_2Cl_{10}] it was specific for each of 4 crystallographically independent cations (65.6°, 71.9°, 88.1°, 89.6° [27]). For comparison, in (2-(2,4-dinitrobenzyl)pyridineH)Cl (TAVMEJ) both rings were nearly perpendicular (89.1° [28]). Thus, this structural feature is heavily dependent on the type of substituents and counterions.

The comparison of both salts to unprotonated 2-arylpyridines containing a bridge between pyridine and phenyl ring exhibits the increase of the C(6)–N(1)–C(2) angle upon protonation: 118.8(2)° in 2-(1-phenylbenzyl)pyridine (YANRAG) [29], 116.8(2)° in 2-benzoylpyridine (NOGCIV) [30] or 117.5(2)° in 2-phenylaminopyridine (NARYEK) [31] → 124.0(5)° or 123.8(5)° [27] in 2bzpyH$^+$.

The $AuCl_4^-$ anions are square-planar; the mean Au–Cl bond lengths are 2.276(2) Å, being nearly the same as in (pyridineH)[$AuCl_4$] (BENYAU: 2.270(2) Å [32]), (3-phenylpyridineH)[$AuCl_4$] (PUHYIB: 2.276(1) Å [33]) and (2,6-diphenylpyridineH)[$AuCl_4$] (ZAKXIS: 2.276(1) Å [34]). Generally, the presently studied (2bzpyH)[$AuCl_4$] salt is similar also to some other (azineH)[$AuCl_4$] ionic pairs, consisting of distinct N-protonated azinium cations and tetrachloraurate anions, the best examples being the X-ray studied species (2-((4-phenyl-1H-1,2,3-triazol-1-yl)methyl)pyridineH)[$AuCl_4$] [35], (1,3-bis(2-pyridyl)benzeneH)[$AuCl_4$] [36], (2,9-di-*n*-butyl-1,10-phenanthrolineH)[$AuCl_4$] and (2,9-di-*sec*-butyl-1,10-phenanthrolineH)[$AuCl_4$] [37].

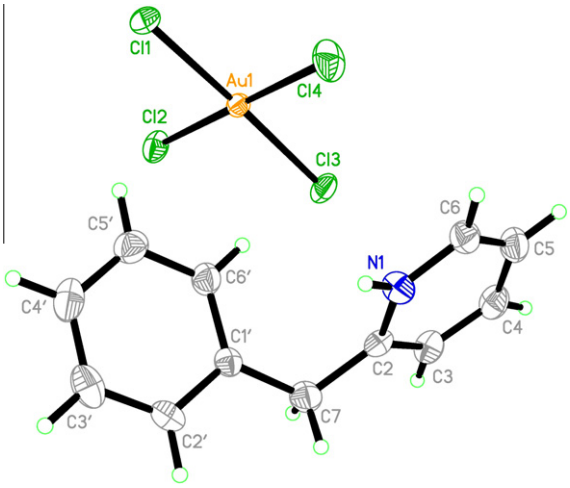


Fig. 1. The (2bzpyH)[AuCl4] salt (PLATON [26]).

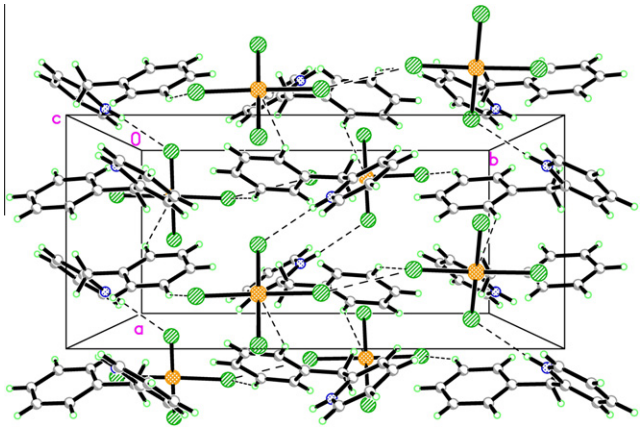


Fig. 2. The packing of the (2bzpyH)[AuCl4] salt in the crystal lattice (PLATON [26]).

In the crystal lattice, the chain of nearly linear intermolecular N(1)–H(1)···Cl(2) [$x+1,y,z$] hydrogen bonds along the crystallographic X axis is formed, with the N(1)···Cl(2) distance of 3.320 Å and the N(1)-H(1)···Cl(1) angle of 165.4°. Some other interactions are: C(5)–H(5)···Cl(1) [$-1/2+x,y,1/2-z$] (with C(5)···Cl(1) 3.595 Å, C(5)–H(5)···Cl(1) 150.4°) and C(3′)–H(3′)···Cl(1) [$1-x,1-y,-z$] (with C(3′)···Cl(3′) 3.713 Å, C(3′)–H(3′)···Cl(1) 155.1°), as well as C(7)–H(7a)···C(4′) [$1-x,1-y,-z$] (with C(7)···C(4′) 3.858 Å, C(7)–H(7a)···C(4′) 171.4°; this contact concerns only one of the two methylene protons).

3.2. ^{1}H NMR spectroscopy

The (2bzpyH)[$AuCl_4$] salt is slightly soluble in $CDCl_3$, CD_2Cl_2 and CD_3CN, and much better in DMSO-d_6. Its ^{1}H NMR spectra in all solvents (Table 3) are noticeably different from those of unprotonated 2bzpy; however, addition of the free ligand results in only one set of ^{1}H signals at intermediate chemical shifts, indicating fast proton exchange between 2bzpyH$^+$ and 2bzpy.

The 2bzpy protonation results in the moderate ^{1}H deshielding (mean $\Delta_{prot}^{H(3)-H(6),H(2')-H(6')}$: 0.28–0.35 ppm), analogous to that for (2bzpyH)[B(3,5-bis(trifluoromethyl)phenyl)$_4$] (mean $\Delta_{prot}^{H(3)-H(6),H(2')-H(6')}$: 0.13 ppm, as deduced from the unassigned ^{1}H NMR data: 8.23, 8.05, 7.74, 7.55, 3 × (7.39 – 7.42),

Table 2
Geometry of $(2bzpyH)^+$, in crystalline (2bzpyH)[$AuCl_4$] and $(2bzpyH)_4[Sb_2Cl_{10}]$ [27].

Bond length	(2bzpyH)[$AuCl_4$]/$(2bzpyH)_4[Sb_2Cl_{10}]$[a] [27] (Å)	Angle	(2bzpyH)[$AuCl_4$]/$(2bzpyH)_4[Sb_2Cl_{10}]$[a] [27] (°)
N(1)–C(2)	1.351(6)/1.33(1)	N(1)–C(2)–C(3)	116.5(5)/117(1)
C(2)–C(3)	1.371(8)/1.37(1)	C(2)–C(3)–C(4)	120.9(5)/120(1)
C(3)–C(4)	1.363(8)/1.37(1)	C(3)–C(4)–C(5)	120.5(6)/121(1)
C(4)–C(5)	1.381(9)/1.36(1)	C(4)–C(5)–C(6)	118.0(7)/118(1)
C(5)–C(6)	1.356(8)/1.35(1)	C(5)–C(6)–N(1)	120.0(6)/120(1)
C(6)–N(1)	1.334(7)/1.33 (1)	C(6)–N(1)–C(2)	124.0(5)/124(1)
C(2)–C(7)	1.491(7)/1.50(1)	N(1)–C(2)–C(7)	119.8(5)/117(1)
C(7)–C(1′)	1.498(7)/1.50(1)	C(3)–C(2)–C(7)	123.7(5)/126(1)
C(1′)–C(2′)	Mean[b]	C(2)–C(7)–C(1′)	118.0(5)/116(1)
C(1′)–C(6′)	1.390(7)/1.38(1)		
C(2′)–C(3′)	Mean[b]	C(7)–C(1′)–C(2′)	Mean[b]
C(6′)–C(5′)	1.368(8)/1.38(1)	C(7)–C(1′)–C(6′)	121.5(5)/121(1)
C(3′)–C(4′)	Mean[b]	C(2′)–C(1′)–C(6′)	116.6(5)/118(1)
C(5′)–C(4′)	1.376(9)/1.35(1)		
		C(1′)–C(2′)–C(3′)	Mean[b]
		C(1′)–C(6′)–C(5′)	121.6(6)/121(1)
		C(2′)–C(3′)–C(4′)	Mean[b]
		C(6′)–C(5′)–C(4′)	120.6(7)/120(1)
		C(3′)–C(4′)–C(5′)	118.8(6)/120(1)

[a] Averaged for four crystallographically different $2bzpyH^+$ cations and round to 0.01 Å or 1°.
[b] Averaged for the formally equivalent (due to the rotation around the C(7)–C(1′) bond) C(1′)–C(2′)–C(3′)–C(4′) and C(1′)–C(6′)–C(5′)–C(4′) halves of the phenyl ring.

Table 3
^1H chemical and protonation/coordination shifts (in parentheses) for 2bzpy, (2bzpyH)[$AuCl_4$], [$Au(2bzpy)Cl_3$], *trans*-[$Pd(2bzpy)_2Cl_2$], [$Au(2bzpy^*)Cl_2$].

Compound	H(3)	H(4)	H(5)	H(6)	H(2′)	H(3′)	H(4′)	H(5′)	H(6′)	CH_2
$2bzpy^{CDCl3}$	7.09	7.55	7.08	8.53	7.25	7.28	7.20			4.15
$2bzpy^{CD2Cl2}$	7.18	7.63	7.15	8.55	7.31	7.33	7.24			4.18
$2bzpy^{CD3CN}$	7.21	7.64	7.16	8.50	7.30	7.31	7.23			4.13
$2bzpy^{DMSO\text{-}d6}$	7.25	7.69	7.20	8.48	7.27	7.28	7.18			4.08
$(2bzpyH)[AuCl_4]^{CDCl3}$	7.71	8.42	7.89	8.85	7.30	7.42	7.39			4.56
	(+0.62)	(+0.87)	(+0.81)	(+0.32)	(+0.05)	(+0.14)	(+0.19)			(+0.41)
$(2bzpyH)[AuCl_4]^{CD2Cl2}$	7.77	8.46	7.92	8.80	7.37	7.45	7.42			4.56
	(+0.59)	(+0.83)	(+0.77)	(+0.25)	(+0.06)	(+0.12)	(+0.18)			(+0.38)
$(2bzpyH)[AuCl_4]^{CD3CN}$	7.82	8.47	7.86	8.50	7.32	7.42	7.38			4.42
	(+0.61)	(+0.83)	(+0.70)	(0.00)	(+0.02)	(+0.11)	(+0.15)			(+0.29)
$(2bzpyH)[AuCl_4]^{DMSO\text{-}d6}$	7.83	8.41	7.84	8.81	7.34	7.37	7.29			4.35
	(+0.58)	(+0.72)	(+0.64)	(+0.33)	(+0.07)	(+0.09)	(+0.11)			(+0.27)
$[Au(2bzpy)Cl_3]^{CDCl3}$ [a]	7.36	7.96	7.54	8.67	7.27	7.40	7.33			4.72
	(+0.27)	(+0.41)	(+0.46)	(+0.14)	(+0.02)	(+0.12)	(+0.13)			(+0.57)
trans-$[Pd(2bzpy)_2Cl_2]^{CDCl3}$ [b]	A 6.94	A + B 7.57	A 7.20	A 9.04	A + B 7.32	A + B 7.43	A + B 7.40			A 5.27
	(−0.15)	(+0.02)	(+0.12)	(+0.51)	(+0.07)	(+0.15)	(+0.20)			(+1.12)
A + B 1:1	B 6.88		B 7.17	B 8.89						B 5.42
	(−0.21)		(+0.09)	(+0.36)						(+1.27)
$[Au(2bzpy^*)Cl_2]^{CDCl3}$	7.68	8.01	7.50	9.32	No proton	7.60	7.08	7.16	7.11	4.55, 4.03
	(+0.59)	(+0.46)	(+0.42)	(+0.79)		(+0.32)	(−0.12)	(−0.12)	(−0.14)	(+0.40/−0.12)
$[Au(2bzpy^*)Cl_2]^{CD2Cl2}$ [c]	7.72	8.04	7.52	9.27	No proton	7.55	7.09	7.18	7.18	4.56, 4.07
	(+0.54)	(+0.41)	(+0.37)	(+0.72)		(+0.22)	(−0.15)	(−0.15)	(−0.13)	(+0.38/−0.11)
$[Au(2bzpy^*)Cl_2]^{CD3CN}$	7.81	8.11	7.56	9.16	No proton	7.48	7.08	7.18	7.22	4.56, 4.20
	(+0.60)	(+0.47)	(+0.40)	(+0.66)		(+0.17)	(−0.15)	(−0.13)	(−0.08)	(+0.43/+0.07)
$[Au(2bzpy^*)Cl_2]^{DMSO\text{-}d6}$ [d]	8.00	8.26	7.71	9.17	No proton	7.41	7.07	7.18	7.25	4.60, 4.36
	(+0.75)	(+0.57)	(+0.51)	(+0.69)		(+0.13)	(−0.11)	(−0.10)	(−0.02)	(+0.52/+0.28)

Literature data for:
[a] $[Au(2bzpy)Cl_3]$ in $CDCl_3$: H(6) 8.69, CH_2 4.73 ppm [1].
[b] *trans*-$[Pd(2bzpy)_2Cl_2]$ in $CDCl_3$: H(6) 8.89/8.74, CH_2 5.35/5.20 ppm [2].
[c] $[Au(2bzpy^*)Cl_2]$ in CD_2Cl_2: H(6) 9.27, others 7.1–8.1, CH_2 4.56, 4.08 ppm [1].
[d] $[Au(2bzpy^*)Cl_2]$ in DMSO-d_6: H(3) 7.99, H(4) 8.26, H(5) 7.71, H(6) 9.17, C_6H_5: 7.41, 2 × (7.14–7.28), 7.07, CH_2 4.62, 4.34 ppm [4].

2 × (7.10 − 7.13) ppm, in $CDCl_3$ [38]). This effect is much stronger for the pyridine ring (mean $\Delta_{prot}^{H(3)-H(6)}$: 0.53–0.66 ppm) than the phenyl one (mean $\Delta_{prot}^{H(2')-H(6')}$: 0.08–0.11 ppm). The deshielding of the nitrogen-adjacent H(6) atom ($\Delta_{prot}^{H(6)}$ = 0.00–0.33 ppm, depending on the solvent; a surprising difference between CD_3CN and the other media should be mentioned) is weaker than for more far-distant pyridine ring protons ($\Delta_{prot}^{H(3)}-\Delta_{prot}^{H(5)}$ = 0.58–0.83 ppm, depending on the solvent). These phenomena and dependencies are probably caused by the electron density decrease due to the delocalization of the positive (+1) electric charge within the whole pyridine ring. The latter hypothesis is supported by the fact that similarly moderate H(6) deshielding was noted for some other 2-substituted pyridinium cations ($\Delta_{prot}^{H(6)}$ = 0.21–0.40 ppm for 2-methylpyridineH$^+$, 2-(*tert*-butyl)pyridineH$^+$, 2-(*tert*-butylmethyl)pyridineH$^+$, 2-(1,1-dimethylbenzyl)pyridineH$^+$ [1,39,40]); Table S1.

The methylene protons in (2bzpyH)[$AuCl_4$] are moderately deshielded (Δ_{prot}^{CH2} = 0.27–0.41 ppm, depending on the solvent), which is again comparable to (2bzpyH)[B(3,5-bis(trifluoromethyl)phenyl)$_4$]

($\Delta^{CH2}_{prot} = 0.23$ ppm, as $\delta^{CH2} = 4.32$ ppm for $2bzpyH^+$ and $\delta^{CH2} = 4.19$ - ppm for 2bzpy, both in $CDCl_3$ [38]).

The $[Au(2bzpy)Cl_3]$ and *trans*-$[Pd(2bzpy)_2Cl_2]$ complexes are soluble and stable in $CDCl_3$, their δ^{H6} and δ^{CH2} parameters being in agreement to the literature values [1,2]. The latter molecule appears in two forms (*ca.* 1:1), being probably rotameric isomers formed by steric hindrance of the bulky 2bzpy ligands, which restricts free rotation around the Pd–N(1) bonds. Such a phenomenon was already mentioned for this compound and its bromide analogue (*trans*-$[Pd(2bzpy)_2Br_2]$ [2]), as well as many other *trans*-$[PdL_2Cl_2]$ complexes with 2-alkyl- or 2-arylpyridines (L = 2-methylpyridine [41], 2,3-dimethylpyridine and 2,4-dimethylpyridine [42], 2-(2-chloroethyl)pyridine [43], 2-(1-methylbenzyl)pyridine [44]). We denote as A and B the species with the H(6) signal at the higher and the lower chemical shift, respectively ($\delta^{H6(A)} > \delta^{H6(B)}$); the order of other proton peaks may be different (e.g. $\delta^{CH2(A)} < \delta^{CH2(B)}$). In our further discussion concerning *trans*-$[Pd(2bzpy)_2Cl_2]$ we will use the weighted (1:1) averages of the Δ^{1H}_{coord} parameters for A and B.

For $[Au(2bzpy)Cl_3]$ the pyridine ring protons are moderately deshielded (mean $\Delta^{H(3)-H(6)}_{coord}$: 0.32 ppm), similarly to $[Au(2ppy)Cl_3]$ (mean $\Delta^{H(3)-H(6)}_{coord}$: 0.36 ppm [21]); this effect is weaker for H(6) than H(3)–H(5) ($\Delta^{H(6)}_{coord} = 0.14$ ppm *vs* $\Delta^{H(3)}_{coord} - \Delta^{H(5)}_{coord} = 0.27$–$0.46$ ppm). It is worth noting that the same coordination shifts pattern was observed for analogous $[AuLCl_3]$ complexes with 2-alkylpyridines (L = 2-methylpyridine [41], 2,3-dimethylpyridine and 2,4-dimethylpyridine [42]). The small H(6) deshielding is comparable to that for $[Au(2ppy)Cl_3]$ ($\Delta^{H(6)}_{coord} = 0.15$ ppm [21]) and $[Au(2\text{-}(1\text{-methylbenzyl})pyridine)Cl_3]$ ($\Delta^{H(6)}_{coord} = 0.08$ ppm [1]); Table S2. These phenomena and dependencies are probably caused by an inductive effect of three electronegative chlorides. The phenyl ring protons are slightly deshielded (mean $\Delta^{H(2')-H(6')}_{coord}$: 0.08 ppm). In consequence, all heterocyclic ring protons are, on average, deshielded as well (mean $\Delta^{H(3)-H(6),H(2')-H(6')}_{coord}$: 0.19 ppm).

For *trans*-$[Pd(2bzpy)_2Cl_2]$ the pyridine ring protons are variously affected (with differences between both rotamers reaching 0.15 ppm); on average, they are slightly deshielded (mean $\Delta^{H(3)-H(6)}_{coord}$: 0.10 ppm). The comparison to *trans*-$[Pd(2ppy)_2Cl_2]$ and *cis*-$[Pd(2ppy)_2Cl_2]$ (mean $\Delta^{H(3)-H(6)}_{coord}$: −0.04 ppm and −0.47 ppm [21]) exhibits the similarity rather to the former than the latter isomer, being in favour of the assumed *trans*-geometry. On the other hand, H(6) is highly deshielded ($\Delta^{H(6)}_{coord} = 0.44$ ppm), in contrast to its slight shielding in *trans*-$[Pd(2ppy)_2Cl_2]$ ($\Delta^{H(6)}_{coord} = -0.12$ ppm) and very large shielding in *cis*-$[Pd(2ppy)_2Cl_2]$ ($\Delta^{H(6)}_{coord} = -0.86$ ppm) [21]; Table S2. For comparison, *cis*-$[Pt(2ppy)_2Cl_2]$ (this complex was originally supposed to have *trans*-geometry but later proved, by single crystal X-ray studies, to be *cis*-isomer (CCDC 799847 [45]) revealed nearly no effect at H(6) ($\Delta^{H(6)}_{coord} = -0.04$ ppm [21]). So complicated ^{1}H NMR coordination shifts patterns derive probably from combination of an inductive effect of two electronegative chlorides and variable anisotropic interactions of the adjacent 2bzpy heterocyclic rings, heavily dependent on complex geometry. The phenyl ring protons are slightly deshielded (mean $\Delta^{H(2')-H(6')}_{coord}$: 0.13 ppm). In consequence, all heterocyclic ring protons are, on average, slightly deshielded as well (mean $\Delta^{H(3)-H(6),H(2')-H(6')}_{coord}$: 0.11 ppm).

The methylene protons in both presently studied complexes are significantly deshielded, much more in *trans*-$[Pd(2bzpy)_2Cl_2]$ than $[Au(2bzpy)Cl_3]$ (Δ^{CH2}_{coord}: 1.20 ppm *vs* 0.57 ppm). A similar dependency was reported for CH protons in *trans*-$[Pd(2\text{-}(1\text{-methylbenzyl})pyridine)_2Cl_2]$ and $[Au(2\text{-}(1\text{-methylbenzyl})pyridine)Cl_3]$ (Δ^{CH}_{coord}: 2.32 ppm *vs* 1.02 ppm [1,44]); Table S2. The difference between CH_2 signals in both rotamers of *trans*-$[Pd(2bzpy)_2Cl_2]$ (−0.15 ppm) has the same absolute magnitude but an opposite sign than in case of H(6).

In DMSO-d_6 both coordination compounds immediately decompose, yielding free 2bzpy. This problem often occurs for Au(III) and Pd(II) chloride–azine complexes and must be always taken into account in this NMR solvent. For example, Fuchita et al., who studied $[Au(2\text{-phenoxypyridine})Cl_3]$ and $[Au(2\text{-}(phenylsulfanyl)pyridine)Cl_3]$ just in DMSO-d_6, erroneously attributed the observed proton signals to the above molecules, although they appeared at the chemical shifts of free ligands, and the same concerned (2-phenoxypyridineH)$[AuCl_4]$ and (2-(phenylsulfanyl)pyridine)$[AuCl_4]$ salts [46]. Most likely, both $[AuLCl_3]$ complexes and LH^+ cations decomposed due to their reactions with DMSO and residual water.

The $[Au(2bzpy^*)Cl_2]$ organometallic is slightly soluble in $CDCl_3$, CD_2Cl_2 and CD_3CN, and well soluble in DMSO-d_6; in contrast to $[Au(2bzpy)Cl_3]$ it does not decompose in the latter solvent. Its δ^{H6} and δ^{CH2} parameters in CD_2Cl_2 and DMSO-d_6 are in agreement to the literature values [1,4]. A similar behaviour was reported for analogous $[Au(LL^*)Cl_2]$ organometallics with many other 2-arylpyridines (LL = 2ppy [19,22,47,48], 2-benzoylpyridine [7,49], 2-phenoxypyridine and 2-phenylsulfanylpyridine [46], 2-phenylaminopyridine and 2-phenyl(*N*-methyl)aminopyridine [46,50]).

In all solvents the ^{1}H NMR pattern of $[Au(2bzpy^*)Cl_2]$ corresponds well to the N(1),C(2′)-cyclometallated structure, revealing eight aromatic protons (four doublets: H(3), H(6), H(3′), H(6′) and four triplets: H(4), H(5), H(4′), H(5′), with the absence of H(2′) and inequivalency of all other phenyl ring hydrogens), as well as two distinct CH_2 atoms. The pyridine ring protons are significantly deshielded (mean $\Delta^{H(3)-H(6)}_{coord}$: 0.51–0.63 ppm, depending on the solvent). In DMSO-d_6, their average deshielding is similar to that for $[Au(2ppy^*)Cl_2]$ (mean $\Delta^{H(3)-H(6)}_{coord}$: 0.63 ppm *vs* 0.55 ppm [22]), and the same concerns H(6) ($\Delta^{H(6)}_{coord}$: 0.69 ppm *vs* 0.86–0.87 ppm [19,22,47,48]). In $CDCl_3$, H(6) is much more deshielded that in $[Au(2bzpy)Cl_3]$ ($\Delta^{H(6)}_{coord}$: 0.79 ppm *vs* 0.14 ppm), such $\Delta^{H(3)}_{coord,[Au(LL^*)Cl2]} \gg \Delta^{H(6)}_{coord,[Au(LL)Cl3]}$ relation being also noted for $[Au(2ppy^*)Cl_2]$ *vs* $[Au(2ppy)Cl_3]$ (0.86–0.87 ppm ≫ 0.15 ppm [19,21,22,47,48]), and for (R)/(S)-$[Au(2\text{-}(1\text{-methylbenzyl})pyridine^*)Cl_2]$ *vs* $[Au(2\text{-}(1\text{-methylbenzyl})pyridine)Cl_3]$ (0.72/0.82 ppm ≫ 0.08 ppm [1]); Table S3.

Similarly high $\Delta^{H(6)}_{coord}$ values were reported for some other $[Au(LL^*)Cl_2]$ organometallics with derivatives of 2ppy (LL = 2-(4-methylphenyl)pyridine, 4-(*n*-propyl)-2-phenylpyridine, 2-(2,4-difluorophenyl)pyridine: $\Delta^{H(6)}_{coord} = 0.86$–$1.13$ ppm [4,48,51]) or 2bzpy (LL = 3-methyl-2-benzylpyridine, 4-methyl-2-benzylpyridine, 5-methyl-2-benzylpyridine, 2-(6-methylbenzyl)pyridine, 2-(5-methylbenzyl) pyridine, 2-(4-methylbenzyl)pyridine, 2-(4-phenylbenzyl)pyridine, 2-(4-chlorobenzyl)pyridine, 2-(1,1-dimethylbenzyl)pyridine, 2-(1-phenylbenzyl)pyridine: $\Delta^{H(6)}_{coord} = 0.45$–$0.82$ ppm [1,7]); Table S3. Thus, this parameter can be regarded as a tool to identify Au(III) cyclometallation of such 2-arylpyridine ligands.

The changes for phenyl ring protons in $[Au(2bzpy^*)Cl_2]$ are of variable sign and moderate or small absolute magnitude, although rather shielding (mean $\Delta^{H(3')-H(6')}_{coord}$: from −0.05 to −0.01 ppm, depending on the solvent). The H(3′) atom, adjacent to the metallated C(2′) carbon, is moderately deshielded while the other protons are weakly shielded ($\Delta^{H(3')}_{coord} = 0.13$–$0.32$ ppm *vs* $\Delta^{H(4')}_{coord} - \Delta^{H(6')}_{coord} = -0.15$ to −0.02 ppm, depending on the solvent). A similar coordination shifts pattern was observed for $[Au(2ppy^*)Cl_2]$ ($\Delta^{H(3')}_{coord} = 0.36$ ppm *vs* $\Delta^{H(4')}_{coord} = -0.11$ to 0.02 ppm [22]). On average, all heterocyclic ring protons are moderately deshielded (mean $\Delta^{H(3)-H(6),H(3')-H(6')}_{coord}$: 0.23–0.30 ppm, depending on the solvent), again similarly to $[Au(2ppy^*)Cl_2]$ (mean $\Delta^{H(3)-H(6),H(3')-H(6')}_{coord}$: 0.30 ppm [22]).

Both methylene protons in $[Au(2bzpy^*)Cl_2]$ become inequivalent and appear as two doublets separated by 0.24–0.52 ppm (δ^{CH2}: 4.45–4.60 ppm *vs* 4.03–4.36 ppm), due to their different orientation in respect to the planes of both rings and the $AuCl_2$ moiety. The same phenomenon was reported for $[Au(4\text{-methyl-}2\text{-benzylpyridine}^*)Cl_2]$ (4.57 ppm *vs* 4.23 ppm), $[Au(5\text{-methyl-}2\text{-benzylpyridine}^*)Cl_2]$ (4.53 ppm *vs* 4.04 ppm) and $[Au(6\text{-methyl-}2\text{-benzylpyridine}^*)Cl_2]$ (4.61 ppm *vs* 4.40 ppm); only in case of $[Au(3\text{-methyl-}2\text{-benzylpyr-}$

idine*)Cl_2] both peaks overlapped (2 × 4.43 ppm) [7]. A similar inequivalency was noted for the two $C(CH_3)_2$ methyl groups in [Au(2-(1,1-dimethylbenzyl)pyridine*)Cl_2] (δ^{CH3}: 2.35 ppm *vs* 2.06 ppm), being also proved by single crystal X-ray studies (ZETYAY [1]). Thus, one can suggest that in [Au(2bzpy*)Cl_2] the methylene protons are not positioned symmetrically in respect to the remaining part of the molecule. On average, they are moderately deshielded (mean Δ^{CH2}_{coord}: 0.14–0.40 ppm, depending on the solvent), however, much less than in [Au(2bzpy)Cl_3] (Δ^{CH2}_{coord}: 0.57 ppm).

3.3. ^{13}C and ^{15}N NMR spectroscopy

^{13}C and ^{15}N NMR chemical and protonation/coordination shifts are collected in Tables 4 and 5, respectively.

The protonation of 2bzpy results in variable effects within the pyridine ring: the nitrogen-adjacent C(2) and C(6) atoms are shielded by *ca.* 4–7 ppm, while those of C(3)–C(5) are deshielded by *ca.* 3–9 ppm, the net result being slight deshielding (mean $\Delta^{C(2)-C(6)}_{prot}$: 1.0 ppm); this pattern is similar to that for pyH^+ cations in (pyH)[$GeCl_3$] (IKOFOD) and (pyH)[$As(N_3)_6$] (CAFRAD) [52–55]). Within the phenyl ring, C(1′) is shielded by *ca.* 3 ppm, while the other carbons are deshielded up to *ca.* 1 ppm, the net result being nearly zero (mean $\Delta^{C(1')-C(6')}_{prot}$: −0.1 ppm). The average effect for both heterocyclic rings is negligible (mean $\Delta^{C(2)-C(6),C(1')-C(6')}_{prot}$: 0.4 ppm), while the methylene carbon is shielded by *ca.* 5 ppm.

The Au(III) or Pd(II) complexation of 2bzpy results in the deshielding of pyridine ring carbons, up to *ca.* 5 ppm and *ca.* 3 ppm, respectively (mean $\Delta^{C(2)-C(6)}_{coord}$: 3.2 ppm for [Au(2bzpy)$Cl_3$] and 2.4 ppm for *trans*-[Pd(2bzpy)$_2Cl_2$]). Within the phenyl ring, the quarternary C(1′) atoms have not been detected, while those of C(2′)–C(6′) are deshielded, up to *ca.* 3 ppm and *ca.* 1 ppm. The methylene carbons are deshielded up to *ca.* 1 ppm, similarly to *cis*-[Pt(2bzpy)(CO)(C_6F_5)$_2$] and [Pt(2bzpy)(C_6F_5)$_3$]$^-$ (Δ^{CH2}_{coord} = 0.2–0.3 ppm [56,57]).

For [Au(2bzpy*)Cl_2] the ^{13}C NMR spectra were measured in all solvents. The most characteristic is the large deshielding of C(2′) ($\Delta^{C2'}_{coord}$ = *ca.* 12–13 ppm), being the overall result of carbon deprotonation and its subsequent auration; it is weaker than for [Au(2ppy*)Cl_2] ($\Delta^{C(2')}_{coord}$ = 26.2 ppm [22]). This effect is different from that for *cis*-[Pt(2bzpy)(C_6F_5)$_2$], where the same C(2′) atom remained protonated and the 2bzpy molecule was bound to Au(III) by η^2-arene interaction (HASMUJ [56]), which resulted in C(2′) shielding by *ca.* 13 ppm [56]. The other phenyl ring carbons are variously affected: the quartenary C(1′) atom is shielded by *ca.* 8–9 ppm, while the CH ones can be either deshielded or shielded; the net result for the whole ring is deshielding (mean $\Delta^{C(1')-C(6')}_{coord}$: 1.5–1.6 ppm). Within the pyridine ring, the quarternary C(2) atom is shielded by *ca.* 5 ppm, while the CH ones are deshielded by *ca.* 3–7 ppm; the net result is deshielding (mean $\Delta^{C(1)-C(6)}_{coord}$: 2.0–2.3 ppm). On average, all heterocyclic ring carbons are deshielded as well (mean $\Delta^{C(2)-C(6),C(1')-C(6')}_{coord}$: 1.7–1.8 ppm). The same phenomenon was noted for [Au(2ppy*)Cl_2], where the average carbon deshielding was *ca.* 6.3 ppm for the phenyl ring, *ca.* 4.1 ppm for the pyridine ring, and *ca.* 5.3 ppm for the whole molecule [22].

The methylene carbon is deshielded by *ca.* 2–3 ppm, this effect being comparable to some [Au(2bzpy*)(XX)] organometallics (XX = phtalimidate, saccharinate, isatinate, benzene-1,2-diacetamidate; Δ^{CH2}_{coord} = 2.7–2.9 ppm [15,16]).

The protonation of 2bzpy results in significant N(1) shielding ($|\Delta^{N(1)}_{coord}|$ = 97.9 ppm), which is typical for azines [58]. It proves that the $2bzpyH^+$ cations remain stable in DMSO-d_6, and do not undergo hydrolysis with residual water present in this NMR solvent.

Table 5
^{15}N chemical and protonation/coordination shifts (in parentheses) for 2bzpy, (2bzpyH)[$AuCl_4$], [Au(2bzpy)Cl_3], *trans*-[Pd(2bzpy)$_2Cl_2$], [Au(2bzpy*)Cl_2].

Compound	N(1)
$2bzpy^{CDCl3}$	−64.7
$2bzpy^{DMSO\text{-}d6}$	−60.9
$(2bzpyH)[AuCl_4]^{DMSO\text{-}d6}$	−158.8 (−97.9)
$[Au(2bzpy)Cl_3]^{CDCl3}$	−148.6 (−83.9)
trans-$[Pd(2bzpy)_2Cl_2]^{CDCl3}$	A −159.4 (−94.7)
A + B 1:1	B −158.7 (−94.0)
$[Au(2bzpy^*)Cl_2]^{DMSO\text{-}d6}$	−151.8 (−90.9)

Table 4
^{13}C chemical and protonation/coordination shifts (in parentheses) for 2bzpy, (2bzpyH)[$AuCl_4$], [Au(2bzpy)Cl_3], *trans*-[Pd(2bzpy)$_2Cl_2$], [Au(2bzpy*)Cl_2].

Compound	C(2)	C(3)	C(4)	C(5)	C(6)	C(1′)	C(2′)	C(3′)	C(4′)	C(5′)	C(6′)	CH_2
$2bzpy^{CDCl3}$	161.1	123.2	136.7	121.4	149.5	139.6	129.2	128.7	126.5			44.9
$2bzpy^{CD2Cl2}$	161.5	123.4	136.8	121.7	149.8	140.4	129.6	129.0	126.8			45.1
$2bzpy^{CD3CN}$	162.1	124.0	137.6	122.4	150.3	141.3	130.1	129.5	127.3			45.2
$2bzpy^{DMSO\text{-}d6}$	160.5	123.0	136.6	121.4	149.1	139.8	128.9	128.3	126.1			43.7
$(2bzpyH)[AuCl_4]^{DMSO\text{-}d6}$	155.9	126.9	145.6	124.6	142.6	136.4	128.9	129.0	127.3			38.9
	(−4.6)	(+3.9)	(+9.0)	(+3.2)	(−6.5)	(−3.4)	0	(+0.7)	(+1.2)			(−4.8)[a]
$[Au(2bzpy)Cl_3]^{CDCl3}$	161.8	128.5	142.0	125.8	149.7	n.d.	130.4	129.8	129.5			45.2
	(+0.7)	(+5.3)	(+5.3)	(+4.4)	(+0.2)		(+1.2)	(+1.1)	(+3.0)			(+0.3)
trans-	A	A + B	A + B	A + B	A + B	n.d.	A + B	A + B	A + B			A 45.6
$[Pd(2bzpy)_2Cl_2]^{CDCl3}$	163.9	126.2	138.5	122.8	152.4		130.4	129.2	127.4			
	(+2.8)	(+3.0)	(+1.8)	(+1.4)	(+2.9)		(+1.2)	(+0.5)	(+0.9)			(+0.7)
A + B 1:1	B											B 46.5
	163.6											
	(+2.5)											(+1.6)
$[Au(2bzpy^*)Cl_2]^{CDCl3}$	156.2	126.2	142.4	124.7	152.4	130.5	141.9	133.5	128.1	128.6	128.6	48.1
	(−4.9)	(+3.0)	(+5.7)	(+3.3)	(+2.9)	(−9.1)	(+12.7)	(+4.8)	(+1.6)	(−0.1)	(−0.6)	(+3.2)
$[Au(2bzpy^*)Cl_2]^{CD2Cl2}$	156.5	126.8	143.0	125.1	152.6	131.4	142.3	133.6	128.1	128.9	129.1	48.3
	(−5.0)	(+3.4)	(+6.2)	(+3.4)	(+2.8)	(−9.0)	(+12.7)	(+4.6)	(+1.3)	(−0.1)	(−0.5)	(+3.2)
$[Au(2bzpy^*)Cl_2]^{CD3CN}$	157.0	127.6	144.3	125.6	153.0	132.9	142.5	133.9	128.3	129.3	129.8	47.9
	(−5.1)	(+3.6)	(+6.7)	(+3.2)	(+2.7)	(−8.4)	(+12.4)	(+4.4)	(+1.0)	(−0.2)	(−0.3)	(+2.7)
$[Au(2bzpy^*)Cl_2]^{DMSO\text{-}d6}$	155.7	126.4	143.3	124.5	152.1	131.9	141.1	132.7	126.9	127.9	128.6	46.1
	(−4.8)	(+3.4)	(+6.7)	(+3.1)	(+3.0)	(−7.9)	(+12.2)	(+4.4)	(+0.8)	(−0.4)	(−0.3)	(+2.4)

[a] Signal overlapping with residual DMSO peak (38.9–40.1 ppm), was observed by DEPT.

The Au(III) and Pd(II) complexation also leads to large N(1) shielding ($|\Delta^{N(1)}_{coord}|$ = 83.9 and 94.0/94.7 ppm, respectively), this effect being *ca.* 10 ppm weaker for [Au(2bzpy)Cl_3] than *trans*-[Pd(2bzpy)$_2Cl_2$]. The same dependency was reported for many other [AuLCl_3] and *trans*-[PdL_2Cl_2] complexes with N(1)-monodentately bonded azines (L = pyridine; 2-, 3- and 4-methylpyridine; 2,3-, 2,4-, 3,5- and 2,6-dimethylpyridine; 2,4,6-trimethylpyridine; 2-, 3- and 4-phenylpyridine [21,41,42,59,60]).

In case of [Pd(2bzpy)$_2Cl_2$], the difference of $\delta^{N(1)}$ (or $\Delta^{N(1)}_{coord}$) parameters between both forms is less than 1 ppm, which excludes the possibility these are two different geometric isomers. Furthermore, their N(1) shielding is much closer to that for *trans*-[Pd(2ppy)$_2Cl_2$] than *cis*-[Pd(2ppy)$_2Cl_2$] ($|\Delta^{N(1)}_{coord}|$ = 94.0/94.7 ppm *vs* 90.4 ppm and 82.9 ppm [21]), confirming the suggested *trans*-geometry; it is well known that ^{15}N shielding effects in platinide(II) chloride–azine complexes are mainly determined by the type of a donor atom in the *trans*-position in respect to a given nitrogen, being larger for *trans*-[PdL_2Cl_2] than *cis*-[PdL_2Cl_2] species [61,62]. Thus, both forms are the same *trans*-[Pd(2bzpy)$_2Cl_2$] isomer, and are probably rotamers, for which anisotropic effects have only a slight influence at ^{15}N shielding. Hence, the ^{15}N NMR spectrum of this complex is a final proof for its *trans*-geometry, this problem being important from the viewpoint of predicting its catalytic applications [5]. In fact, the geometry of [Pd(2bzpy)$_2Cl_2$] was never evidenced due to the lack of the respective X-ray structure, and was only suggested on the basis of ambiguous far-IR spectra: two ν_{Pd-Cl} bands, observed at 340 and 336 cm^{-1} (by Hiraki et al. at 352 and 344 cm^{-1} [2]), could potentially derive either from two *trans*-rotamers or from one *cis*-isomer. Generally, for platinide(II) chloride–azine complexes far-IR spectroscopy is an important tool for geometry determination, but it can be misleading, not allowing to judge between *trans*- and *cis*-species; as an example may serve the recently studied [Pt(2ppy)$_2Cl_2$] complex, which originally seemed to have *trans*-geometry (due to the observation of one ν_{Pt-Cl} band at 333 cm^{-1}; the respective ^{15}N NMR spectrum was not measured because of low solubility [21]), but finally proved to be *cis*-[Pt(2ppy)$_2Cl_2$] (by single crystal X-ray studies, CCDC 799847 [45]).

In [Au(2bzpy*)Cl_2] the N(1) atom is *ca.* 7 ppm more shielded than in [Au(2bzpy)Cl_3] ($|\Delta^{N(1)}_{coord}|$ = 90.9 ppm *vs* 83.7 ppm), in contrast to the pair of [Au(2ppy*)Cl_2] and [Au(2ppy)Cl_3], where the ^{15}N shielding effects were nearly the same (77.0 ppm *vs* 77.6 ppm [21,22]).

4. Conclusions

2-benzylpyridine (2bzpy) forms three principal types of Au(III) and Pd(II) compounds: salts containing protonated 2bzpyH$^+$ cations, complexes with N(1)-monodentately bonded 2bzpy ligands (e.g. [Au(2bzpy)Cl_3], *trans*-[Pd(2bzpy)$_2Cl_2$]), and organometallics with the N(1),C(2′)-cyclometallated monoanionic 2bzpy* ligands, deprotonated in the benzyl side group at the *ortho*-carbon C(2′) (e.g. [Au(2bzpy*)Cl_2]).

The X-ray structure of 2-benzylpyridinium tetrachloraurate(III) exhibits it is a typical ionic pair, consisting of distinct 2bzpyH$^+$ cations and $[AuCl_4]^-$ anions. The ^{1}H, ^{13}C and ^{15}N NMR spectra of [Au(2bzpy)Cl_3], *trans*-[Pd(2bzpy)$_2Cl_2$] and [Au(2bzpy*)Cl_2] reveal some interesting dependencies between the respective Δ^{1H}_{coord}, Δ^{13C}_{coord}, Δ^{15N}_{coord} coordination shifts and the molecular structures. For [Au(2bzpy*)Cl_2] the most characteristic phenomenon is the large deshielding of the nitrogen-adjacent H(6) proton and of the metallated C(2′) carbon, as well as even more significant shielding of the coordinated N(1) nitrogen; the latter effect occurs also for 2bzpyH$^+$, [Au(2bzpy)Cl_3] and *trans*-[Pd(2bzpy)$_2Cl_2$]. The ^{1}H, ^{13}C and ^{15}N NMR signals of *trans*-[Pd(2bzpy)$_2Cl_2$] are duplicate but differ only slightly, confirming the presence of two rotational isomers; the comparison of their Δ^{15N}_{coord} parameters to the literature values for analogous Pd(II) complexes having the known structure allows to prove *trans*-geometry suggested previously on the basis of far-IR studies.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2012.08.005.

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