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Organometallic palladium(II) complexes with *N*-((pyridin-2-yl)methylene)-4-amino-2,1,3-benzothiadiazole: synthesis, characterization and reactivity

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ABSTRACT

Palladium(II) chloro– and methyl-complexes with *N*-((pyridin-2-yl)methylene)-4-amino-2,1,3-benzothiadiazole in the coordination sphere were synthesized from 4-amino-2,1,3-benzothiadiazole, pyridine-2-carboxaldehyde and suitable metal precursors. According to experimental outcomes and DFT calculations, the ligand interacts with the metal centre through the pyridine and imine nitrogen atoms, while the benzothiadiazole heterocycle remains as a free pendant. The methyl-complex was reacted with CO in mild conditions affording the related acyl-complex, whose structure was unambiguously determined by X-ray diffraction. All the complexes revealed to be catalytically active towards the methoxycarbonylation of iodobenzene to methyl benzoate.

1. Introduction

2,2′:6′,2″-terpyridine (tpy) is one of the most investigated nitrogen-donor ligands in coordination, organometallic and materials chemistry, with noticeable applications of its metal derivatives in catalysis [1–4]. Tpy forms stable complexes with d^8 transition metal centres such as palladium(II) and platinum(II), whose structures and reactivity were deeply investigated in the past [5–15]. This family of coordination compounds found application in different fields, such as bioinorganic chemistry [16–28], analytical chemistry [29–32], supramolecular chemistry [33–41] and catalysis [42–48]. The versatile properties of tpy-based complexes opened up the study on coordination compounds bearing structurally comparable tridentate N-donors, such as 2,6-bis(pyrazolyl)pyridine, 2,6-di(8-quinolyl)pyridine, 2,5-bis(α-pyridyl)pyrrolate and their derivatives [49–53].

In this context, imine ligands derived from the condensation of 8-aminoquinoline and N-heterocycles with aldehydo- or keto-substituents in *ortho* position are characterized by electronic and steric features somewhat comparable to tpy [54–57]. Several palladium(II) and platinum(II) complexes with π-extended [N,N',N'']-donor ligands formed by metal-assisted condensation of 8-aminoquinoline with pyridine-2-carboxaldehyde, 2-acetyl-pyridine, 2-benzoyl-pyridine, thiazole-2-carboxaldehyde and imidazole-4-carboxaldehyde were prepared in the past. Reactivity studies highlighted the influence of the different five-membered heterocycles on the behaviour of the corresponding complexes [58,59]. The one-pot approach was also applied by Sun and co-workers for the preparation of a series of iron(II), cobalt(II) and nickel(II) halide complexes with *N*-((pyridin-2-yl)methylene)quinolin-8-amine, that exhibited noticeable catalytic activities for ethylene oligomerization after activation by organoaluminum derivatives [60,61]. Recently, the metal-assisted condensation of pyrrole-2-aldehyde and 8-aminoquinoline in the presence of [M(CH_3)Cl(COD)] [*M* = Pd, Pt; COD = 1,5-cyclooctadiene] afforded in a single step neutral palladium(II) and platinum(II) chloro–complexes with the conjugate base of [(pyrrol-2-yl)methylene]quinolin-8-amine, thanks to the metal-assisted condensation followed by the protonolysis of the metal-carbon bond by the pyrrole NH [62].

With the aim of synthesizing new d^8 metal complexes with tpy-like ligands in the coordination sphere, the investigation was pointed towards the replacement of the quinoline fragment with other π-extended N-donors. The attention was focused on 2,1,3-benzothiadiazole (BTD), a versatile compound of growing interest thanks to its photophysical properties [63,64] and exploited

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for the preparation of polymers, aggregates, organic semiconductors and liquid crystals for advanced technology [65–70]. The organic chemistry of thiadiazoles was subjected to noticeable developments in recent years [71]. Moreover, BTD and its derivatives revealed to be suitable ligands in coordination chemistry, exhibiting variable coordination modes and sometimes forming luminescent compounds [72]. For instance, bridging BTD between two $\{Ir(C_5Me_5)Cl_2\}$ fragments was observed by X-ray diffraction, and selected substituted derivatives exhibited monodentate, chelating or chelating-bridging coordination towards iridium(III) [73]. Coordination polymers were obtained by reacting BTD with CuCl, CuI and Cu/CuX_2 ($X^- = NO_3^-$, ClO_4^-) [74–76], while aryl-substituted BTD formed luminescent cyclometalated complexes with palladium(II) [77]. Another luminescent derivative was isolated from the reaction between $ZnCl_2$ and a β-ketoimine-functionalized BTD [78]. Chelate complexes of divalent first-row transition metal centres were formed with BTD-based salicylaldiminates [79,80], and a BTD-conjugated naphthol hydrazone recently revealed to be an excellent fluorescent sensor towards iron(III) [81]. A near-infrared luminescent probe for the detection of mercury(II) was prepared by coupling the triphenylamine-BTD fluorophore and rhodanine-3-acetic acid as the recognizing group [82]. Transition metal complexes based on ruthenium(II) and osmium(II) with BTD in the coordination sphere were successfully applied as molecular probes for CO detection [83–86].

Our research group recently improved the synthesis of 4-amino-2,1,3-benzothiadiazole [87], and its structural similarity with 8-aminoquinoline prompted us to verify the possibility of metal-assisted condensation with N-heterocyclic aldehydes in the presence of d^8 metal precursors. In particular, here we report the synthesis, characterization and catalytic activity towards the methoxycarbonylation of iodobenzene of organometallic palladium(II) complexes with *N*-((pyridin-2-yl)methylene)-4-amino-2,1,3-benzothiadiazole (pyN^{BTD}) in the coordination sphere. The structure of the acyl-complex $[Pd(COCH_3)Cl(pyN^{BTD})]$ was elucidated by means of X-ray diffraction.

2. Experimental section

2.1. Materials and methods

Commercial solvents (Merck) were purified following reported procedures [88]. Pyridine-2-carboxaldehyde (Merck) was purified by distillation at 328 K and 0.1 Torr. The other reagents were Merck products used as received. $[PdCl_2(COD)]$, $[Pd(CH_3)Cl(COD)]$ and $[Pd(OAc)_2(phen)]$ (OAc = acetate, phen = 1,10-phenanthroline) were synthesized according to literature procedures [89–91]. 4-Amino-2,1,3-benzothiadiazole (NH_2-BTD) was prepared following a method previously reported by our research group [87]. The syntheses of the complexes were performed using common Schlenk techniques. The pyN^{BTD} ligand was synthesized under inert atmosphere in a glove-box (MBraun Labstar with MB 10 G gas purifier) filled with N_2.

Elemental analyses were carried out using an Elementar Unicube microanalyzer. The chloride content was determined using the Mohr's method [92]. The conductivity of the complexes in solution [93] was measured with a Radiometer Copenhagen CDM83 instrument. Melting point measurements were carried out using a modified Falc 360 D apparatus equipped with a video recording device. IR spectra were collected in the 4000 – 400 cm^{-1} range using a PerkinElmer Spectrum One spectrophotometer. Variable temperature nuclear magnetic resonance (NMR) spectra were collected employing Bruker Avance 300 and Avance 400 instruments operating respectively at 300.13 MHz and 400.13 MHz of ^1H resonance. ^1H and ^{13}C NMR spectra were referred to the partially non-deuterated fraction of the solvent, itself quoted to tetramethylsilane. UV–VIS spectra in dichloromethane were collected using an OceanOptics instrument equipped with a tungsten/deuterium lamp DH-2000-BAL and a UV–VIS-NIR detector HR4000CG. The same detector, coupled with near-UV and visible OceanOptics LED sources, was used for preliminary luminescence investigations. GCMS– analyses were performed using a MSD Agilent Technologies 5977B (electron impact) coupled with Agilent Technologies 7720 gas chromatographer and a HP5-MS 19091S-433UI capillary column (30 m × 0.32 mm × 0.25 μm). The experimental conditions required 1.2 mL min^{-1} helium flow and an initial temperature of 373 K that was kept for 2 min. Then the heating rate was set to 20 K min^{-1} until 573 K and this temperature was kept for 15 min.

2.2. Synthesis and characterization of pyN^{BTD}

All the manipulations were carried out in a glove-box under N_2 atmosphere. NH_2-BTD (0.152 g, 1.0 mmol) was dissolved in 25 mL of dry dichloromethane and 3 Å molecular sieves (about 3.0 g) were added. A stoichiometric amount of freshly distilled pyridine-2-carboxaldehyde (96 μL) was introduced with a microsyringe and the reaction mixture was refluxed for six hours. After cooling at room temperature, the solution was filtered and the solvent was evaporated under reduced pressure. The addition of 10 mL of isohexane caused the separation of an orange powder, that was collected by filtration, washed two times with about 5 mL of isohexane and dried under vacuum. Yield was 95% (0.228 g). The compound revealed to be moisture sensitive, thus the characterization data are limited to the NMR spectra.

pyN^{BTD}. ^1H NMR ($CDCl_3$, 298 K) δ 9.24 (s, 1H, CH=N), 8.78 (d, 1H, $^3J_{HH}$ = 4.6 Hz, py), 8.40 (d, 1H, $^3J_{HH}$ = 7.8 Hz, py), 7.92 (s, 1H, $^3J_{HH}$ = 8.8 Hz, BTD), 7.88 (dd, 1H, $^3J_{HH}$ = 7.8 Hz, py), 7.67 (dd, 1H, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 8.8 Hz, BTD), 7.43 (dd, 1H, $^3J_{HH}$ = 4.6 Hz, $^3J_{HH}$ = 7.8 Hz, py), 7.41 (d, 1H, $^3J_{HH}$ = 7.4 Hz, BTD). ^{13}C NMR ($CDCl_3$, 298 K) δ 164.4 (CH=N), 156.1 (C-ipso), 154.5 (C-ipso), 150.0 (C-ipso), 149.9 (py), 142.9 (C-ipso), 136.7 (py), 130.0 (BTD), 125.6 (py), 122.3 (py), 119.8 (BTD), 119.5 (BTD).

2.3. Synthesis and characterization of $[PdCl_2(pyN^{BTD})]$ and $[Pd(CH_3)Cl(pyN^{BTD})]$

To a solution containing 0.076 g (0.5 mmol) of NH_2-BTD in 30 mL of dry dichloromethane, a stoichiometric amount of freshly distilled pyridine-2-carboxaldehyde (48 μL) was added together with 3 Å molecular sieves. The reaction mixture was refluxed for six hours. After cooling at room temperature, the solution was filtered and added to 0.4 mmol of $[PdCl_2(COD)]$ (0.114 g) or $[Pd(CH_3)Cl(COD)]$ (0.106 g). The reaction mixture was stirred overnight at room temperature, and the product precipitated from CH_2Cl_2 was filtered, washed with 5 mL of fresh CH_2Cl_2 and dried under vacuum. Yield was 81% (0.135 g) for $[PdCl_2(pyN^{BTD})]$ and 90% (0.143 g) for $[Pd(CH_3)Cl(pyN^{BTD})]$.

$[PdCl_2(pyN^{BTD})]$. Anal. calcd for $C_{12}H_8Cl_2N_4PdS$ (417.60 g mol^{-1},%): C, 34.51; H, 1.93; N, 13.42; S, 7.68; Cl, 16.98. Found (%): C, 34.37; H, 1.94; N, 13.37; S, 7.65; Cl, 17.05. M.p. > 500 K. Λ_M (DMSO, 298 K): 3 ohm^{-1}mol^{-1}cm^2. ^1H NMR (CD_3NO_2, 298 K) δ 9.28 (d, 1H, $^3J_{HH}$ = 5.2 Hz, py), 8.80 (s, 1H, CH=N), 8.40 (t, 1H, $^3J_{HH}$ = 7.7 Hz, arom), 8.23 (d, ^1H, $^3J_{HH}$ = 7.3 Hz, arom.), 8.11 (d, ^1H, $^3J_{HH}$ = 8.8 Hz, arom.), 7.95 (m, 1H, arom.), 7.82 (t, ^1H, $^3J_{HH}$ = 7.7 Hz, arom.), 7.73 (d, 1H, $^3J_{HH}$ = 7.3 Hz, arom.). IR (KBr, cm^{-1}): 3105–2920 m/w (aromatic ν_{C-H}), 1630–1445 m/w (aromatic ν_{C-C} and ν_{C-N}).

$[Pd(CH_3)Cl(pyN^{BTD})]$. Anal. calcd for $C_{13}H_{11}ClN_4PdS$ (397.19 g mol^{-1},%): C, 39.31; H, 2.79; N, 14.11; S, 8.07; Cl, 8.93. Found (%): C, 39.15; H, 2.80; N, 14.05; S, 8.04; Cl, 8.89. M.p. > 500 K. Λ_M (DMSO, 298 K): 2 ohm^{-1}mol^{-1}cm^2. ^1H NMR (DMSO-d_6, 298 K) δ 9.27 (s, br, 1H, CH=N), 8.83 (s, br, 1H, py), 8.33 (s, br, 1H, py), 8.25

(d, 1H, $^3J_{HH}$ = 7.4 Hz, BTD), 8.10 (d, 1H, $^3J_{HH}$ = 8.0 Hz, BTD), 7.97 (s, br, 1H, py), 7.85 (t, 1H, $^3J_{HH}$ = 7.5 Hz, BTD), 7.68 (s, br, 1H, py), 1.09–0.00 (s, very br, Pd-Me). ^{1}H NMR (DMSO–d_6, 318 K) δ 9.25 (s, 1H, CH=N), 8.84 (d, br, 1H, $^3J_{HH}$ = 4.6 Hz, py), 8.31 (s, br, 1H, py), 8.25 (d, 1H, $^3J_{HH}$ = 7.4 Hz, BTD), 8.07 (d, 1H, $^3J_{HH}$ = 8.0 Hz, BTD), 7.93 (s, br, 1H, py), 7.84 (t, 1H, $^3J_{HH}$ = 7.5 Hz, BTD), 7.67 (s, br, 1H, py), 0.54 (s, br, 3H, Me). IR (KBr, cm^{-1}): 3110–2930 m/w (aromatic ν_{C-H}), 2890–2815 m/w (ν_{C-H}), 1620–1450 m/w (aromatic ν_{C-C} and ν_{C-N}).

2.4. Synthesis and characterization of [Pd{C(O)CH$_3$}Cl(pyN^{BTD})]

A solution containing 0.100 g (0.25 mmol) of [Pd(CH$_3$)Cl(pyN^{BTD})] in 20 mL of dichloromethane was put under 0.1 MPa CO pressure at room temperature. The solid rapidly dissolved in CH_2Cl_2, affording almost immediately a dark red solution. After one hour the solvent was evaporated under reduced pressure and the residual solid was triturated with 10 mL of diethyl ether. The solid was filtered, washed with 2 × 15 mL of diethyl ether and dried under vacuum. Yield: 98% (0.105 g). Crystals suitable for X-ray diffraction were collected from dichloromethane/diethyl ether solutions.

[Pd{C(O)CH$_3$}Cl(pyN^{BTD})]. Anal. calcd for $C_{14}H_{11}ClN_4OPdS$ (425.20 g mol^{-1},%): C, 39.55; H, 2.61; N, 13.18; S, 7.54; Cl, 8.34. Found (%): C, 39.39; H, 2.62; N, 13.13; S, 7.51; Cl, 8.37. M.p. 473 K (dec.). Λ_M (acetone, 298 K): 1 ohm^{-1}mol^{-1}cm^2. ^{1}H NMR ($CDCl_3$, 298 K) δ 9.62 (s, br, 1H, CH=N), 8.95 (s, br, 1H, py), 8.54 (s, br, 1H, py), 8.47 (s, br, 1H, py), 8.15 (m, br, py), 7.99 (d, 1H, $^3J_{HH}$ = 9.0 Hz, BTD), 7.93 (d, 1H, $^3J_{HH}$ = 7.5 Hz, BTD), 7.71 (dd, 1H, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 9.0 Hz, BTD), 2.71 (s, 3H, Pd-COCH$_3$). ^{13}C NMR ($CDCl_3$, 298 K) δ 164.6 (CH=N), 156.0 (C-ipso), 151.1 (py), 148.5 (C-ipso), 139.2 (py), 131.2 (C-ipso), 130.8 (C-ipso), 129.5 (BTD), 128.9 (BTD), 122.0 (BTD), 35.6 (CO$\underline{C}$H$_3$), C=O not detected. IR (KBr, cm^{-1}): 3130–2970 m/w (aromatic ν_{C-H}), 2920–2815 m/w (ν_{C-H}), 1697s ($\nu_{C=O}$), 1600–1470 m (aromatic ν_{C-C} and ν_{C-N}). UV–VIS (CH_2Cl_2, r.t., nm): < 500, 256, 316 (max), 359, 372 (sh), 395 (sh).

2.5. X-ray structure determination

Crystallographic data were collected at CACTI (Universidade de Vigo) at 100 K (CryoStream 800) using a Bruker D8 Venture Photon II CMOS detector and Mo-Kα radiation (λ = 0.71073 Å) generated by an Incoatec Microfocus Source IμS. The software APEX3 [94] was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT [94] for integration of intensity of reflections, and SADABS [94] for scaling and empirical absorption correction. The crystallographic treatment was performed with the Oscail program [95] and solved using the SHELXT program [96]. The structure was subsequently refined by a full-matrix least-squares based on F^2, using the SHELXL program [97]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters. Other details concerning crystal data and structure refinement are given in Table 1. CCDC 2236101 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. PLATON (version 60720) was used to obtain some geometrical parameters from the cif file [98].

2.6. Computational details

Geometry optimizations were carried out using the global-hybrid *meta*-NGA DFT functional MN15 [99] in combination with Alhrichs and Weigend's split-valence polarized def2-SVP, with ECP on Pd [100]. The C-PCM implicit solvation model was added to MN15 calculations, considering dichloromethane or dimethyl sulfoxide as implicit solvents [101]. IR simulations were carried out using the harmonic approximation, from which zero-point vibrational energies and thermal corrections (T = 298.15 K) were obtained [102]. The software used was Gaussian 16 [103]. Cartesian coordinates of the DFT-optimized structures are collected in the Supporting information.

Table 1
Crystal data and structure refinement for [Pd{C(O)CH$_3$}Cl(pyN^{BTD})].

Empirical formula	C_{14} H_{11} Cl N_4 O Pd S
Formula weight	425.18
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 11.3051(7) Å b = 6.9256(4) Å c = 19.3392(10) Å β = 100.944(2)°
Volume	1486.62(15) Å^3
Z	4
Density (calculated)	1.900 Mg/m^3
Absorption coefficient	1.574 mm^{-1}
F(000)	840
Crystal size	0.234 × 0.051 × 0.043 mm
Theta range for data collection	3.131 to 28.299°
Index ranges	$-15 \le h \le 15$ $-9 \le k \le 9$ $-25 \le l \le 25$
Reflections collected	34,408
Independent reflections	3676 [R_{int} = 0.0278]
Reflections observed (>2σ)	3445
Data Completeness	0.996
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6534
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3676 / 0 / 200
Goodness-of-fit on F^2	1.088
Final R indices [I>2σ(I)]	R_1 = 0.0169 wR_2 = 0.0417
R indices (all data)	R_1 = 0.0187 wR_2 = 0.0425
Largest diff. peak and hole	0.344 and −0.627 e.Å^{-3}

2.7. Catalytic tests

The reactions were carried out in an autoclave equipped with PTFE insertion, and a pressure regulator to maintain constant the reaction pressure. A circulation bath ensured a stable temperature of around 393 K. In a typical experiment, 0.002 mmol of palladium(II) complex, 1.4 mmol of triethylamine and 0.8 mmol of iodobenzene were dissolved in 20 mL of methanol and introduced into the reactor. After that, the reactor was closed, purged before with nitrogen and then with carbon monoxide, pressurized at 5 MPa and heated to 393 K under stirring for 2 h. Once cooled down to room temperature, the liquid phase was analysed by GC–MS. The selectivity was 100% in all the cases. The activities are expressed as Turnover Numbers, TON, mol_{ester} $mol_{Pd}{}^{-1}$.

3. Results and discussion

Preliminary tests to verify the reactivity of NH_2-BTD towards pyridine-2-carboxaldehyde were carried out by means of NMR spectroscopy in CD_3OD. The related ^{1}H NMR spectra are reported in Figure S1. Differently from 8-aminoquinoline [58], the corresponding hemiaminal (2,1,3-benzothiadiazol-4-ylamino)(pyridin-2-yl)methanol did not form immediately at room temperature on mixing the two reagents at room temperature. After reacting overnight new resonances were however detected, in particular a singlet at 6.03 ppm diagnostic for the formation of the

hemiaminal. The aldehyde resonance almost disappeared, but the related imine formed only in trace amounts, as suggested by the very weak resonance at 9.31 ppm. The NMR measurements underlined the lower reactivity of NH_2-BTD towards pyridine-2-carboxaldehyde compared to 8-aminoquinoline, probably because of the lower nucleophilicity of the amine group induced by the presence of more electron withdrawing groups in the heterocycle. Attempts to force the reaction by reacting NH_2-BTD and pyridine-2-carboxaldehyde in refluxing ethanol were unsuccessful, since a red solid composed of a complex mixture of species separated from the solution.

Evidence for the formation of the corresponding Schiff base *N*-((pyridin-2-yl)methylene)-4-amino-2,1,3-benzothiadiazole (pyN^{BTD}) from the reactants was obtained after prolonged refluxing in dichloromethane (about six hours) in the presence of an excess of 3 Å molecular sieves. Once isolated as an orange solid by filtration of the solution, evaporation of the solvent and addition of isohexane, the product revealed to be unstable under air at room temperature probably because of its interaction with moisture. The work-up was then carried out in glove-box under inert atmosphere. In this way, pyN^{BTD} was isolated in pure form, and the related NMR spectra are shown in Figures S2-S3. The presence of the imine fragment is confirmed by a sharp singlet at 9.24 ppm in the ^1H NMR spectrum, correlated to a $^{13}C\{^1H\}$ NMR resonance at 164.4 ppm. The aromatic region of the ^1H NMR spectrum also shows seven multiplets attributable to the pyridine and BTD heterocycles, while seven aromatic CH signals and four C_{ipso} resonances in the $^{13}C\{^1H\}$ NMR spectrum are in agreement with the proposed formulation. According to the NMR spectra, only one isomer of pyN^{BTD} is formed.

The first attempts to prepare palladium(II) complexes with pyN^{BTD} in the coordination sphere were carried out by reacting NH_2-BTD and pyridine-2-carboxaldehyde in methanol at room temperature in the presence of a stoichiometric amount of $[PdCl_2(COD)]$ or $[Pd(CH_3)Cl(COD)]$, following previously reported procedures [58,59]. Only in the first case a solid characterized as a palladium(II) complex with pyN^{BTD} in the coordination sphere separated in low yield from the reaction mixture, while a mixture of different species was obtained starting from $[Pd(CH_3)Cl(COD)]$. The synthetic procedure was therefore modified, and the palladium(II) precursors were reacted with CH_2Cl_2 solutions containing a stoichiometric mixture of NH_2-BTD and pyridine-2-carboxaldehyde, previously heated to reflux for six hours in the presence of molecular sieves (Scheme 1). According to the elemental analyses, complexes having formulae $[PdCl_2(pyN^{BTD})]$ and $[Pd(CH_3)Cl(pyN^{BTD})]$ separated in good yield as reddish-orange solids from the CH_2Cl_2 solutions.

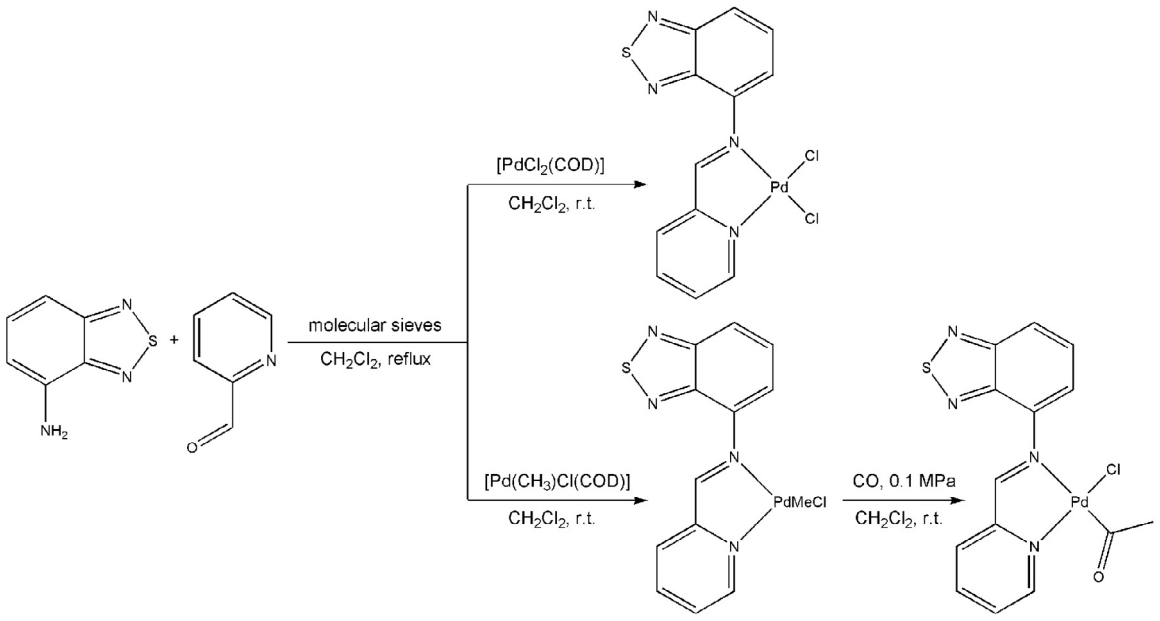
The products revealed to be slightly soluble only in highly polar organic solvents, thus preventing the growth of single crystals suitable for X-ray diffraction. The formation of the coordinated Schiff base was indirectly supported by the IR spectra, where no signal related to aldehyde $\nu_{C=O}$ stretching is detectable (Figure S4). The ^1H NMR spectrum of $[PdCl_2(pyN^{BTD})]$ recorded in CD_3NO_2 (Figure S5) shows in the aromatic region a set of resonances attributable to both the pyridine and BTD heterocycles, together with a singlet at 8.80 ppm related to the imine fragment. The doublet at 9.28 is attributable to the proton in the *ortho* position with respect to the nitrogen atom of the pyridine ring, as suggested by the low $^3J_{HH}$ coupling constant, equal to 5.3 Hz. Unfortunately, the poor solubility did not allow to collect ^{13}C NMR data useful to improve the characterization. The ^1H NMR spectrum of $[Pd(CH_3)Cl(pyN^{BTD})]$ in DMSO–d_6 at 298 K (Figure S6) is also characterized by eight resonances in the aromatic region, three of them associated with the BTD fragment, and the four remaining to the pyridine moiety and the imine proton. The signals are broad, in particular the ones related to pyridine and imine groups, indicating fluxional behaviour. The resonance related to the coordinated methyl group can be hardly detected at 298 K because of its broadness. Heating the solution at 318 K (Figure S6) allowed to observe the singlet centred at 0.54 ppm associated with Pd-CH_3, but some of the signals related to the pyridine fragment resulted too large to be detected at this temperature. Given the scarce solubility and the fluxional behaviour, we were unable to collect useful $^{13}C\{^1H\}$ NMR resonances for $[Pd(CH_3)Cl(pyN^{BTD})]$.

Conductivity measurements on DMSO solutions of $[PdCl_2(pyN^{BTD})]$ and $[Pd(CH_3)Cl(pyN^{BTD})]$ indicated that the compounds are neutral, differently to what was observed in the case of 8-aminoquinoline derivatives [58,59]. The chlorides remain therefore coordinated to palladium(II), and attempts to react the complexes with silver salts caused only the formation of intractable mixtures. To confirm the experimental outcomes, DFT calculations were carried out on all the possible isomers of the two complexes. As observable in Figs. 1 and 2, reporting the optimized geometries in the presence of DMSO as continuous medium, the formation of ionic species was ruled out, since the BTD heterocycle resulted to be less coordinating than the other N-donor moieties and chloride. pyN^{BTD} behaves as a bidentate N-donor through the pyridine and imine nitrogen atoms, with a free BTD pendant. The methyl ligand can be in *trans* position with respect to the imine or pyridine moiety, but as observable in Fig. 2 the Gibbs energy difference between the two isomers is too low (less than 0.1 kcal mol^{-1}) to be conclusive. The previously described fluxional behaviour is perhaps related to the presence in solution of two species with strictly comparable energy in rapid exchange. Despite the overstabilization of the ionic interactions, DFT calculations carried out in *vacuo* confirmed that the preferred coordination mode of pyN^{BTD} is through the imine and the pyridine nitrogen atoms (see Figures S7-S8 for the ground-state geometries and the relative Gibbs energy values).

Despite the presence of the BTD heterocycle, both complexes did not reveal any appreciable luminescence in the visible and near-IR range in solution and at the solid state.

The reaction between $[Pd(CH_3)Cl(pyN^{BTD})]$ and CO (0.1 MPa) at room temperature afforded the corresponding acyl-complex $[Pd\{C(O)CH_3\}Cl(pyN^{BTD})]$ (Scheme 1), as confirmed by the NMR and IR spectra (Figures S9-S11). In particular, the presence of a broad singlet related to the coordinated acyl fragment at 2.71 ppm in the ^1H NMR spectrum (corresponding ^{13}C resonance at 35.6 ppm) and the IR $\nu_{C=O}$ stretching at 1697 cm^{-1} are diagnostic for the insertion of carbon monoxide in the Pd-CH_3 bond. As already described for $[Pd(CH_3)Cl(pyN^{BTD})]$, some of the ^1H NMR aromatic resonances are broadened because of the fluxional behaviour in solution. $[Pd\{C(O)CH_3\}Cl(pyN^{BTD})]$ revealed to be more soluble in organic solvents such as acetone and dichloromethane compared to the other pyN^{BTD} derivatives. Conductivity measurements in acetone confirmed the formation of a neutral species. The UV–Vis spectrum in dichloromethane solution reported in Figure S12 shows several absorptions covering all the UV range and the 400 - 550 nm portion of the visible spectrum, accounting for the intense orange colour observed for the sample both as powder and in concentrated solutions. As for the previously described complexes, no photoluminescence was observed in solution or at the solid state.

Crystals of $[Pd\{C(O)CH_3\}Cl(pyN^{BTD})]$ suitable for X-ray diffraction were collected from dichloromethane/diethyl ether solutions. The molecular structure is shown in Fig. 3 [104]. Selected bond lengths and angles are collected in Table 2. The palladium atom is tetracoordinated in a square planar environment composed of the pyridine and imine moieties of pyN^{BTD}, a chloride ion and an acyl ligand. The coordination of pyN^{BTD} shows quite different Pd-N distances, being the Pd-N_{imine} bond more than 0.2 Å longer compared to the Pd-$N_{pyridine}$ one. It is common that in palladium(II) com-



Scheme 1. Synthesis of palladium(II) pyN^{BTD} complexes.

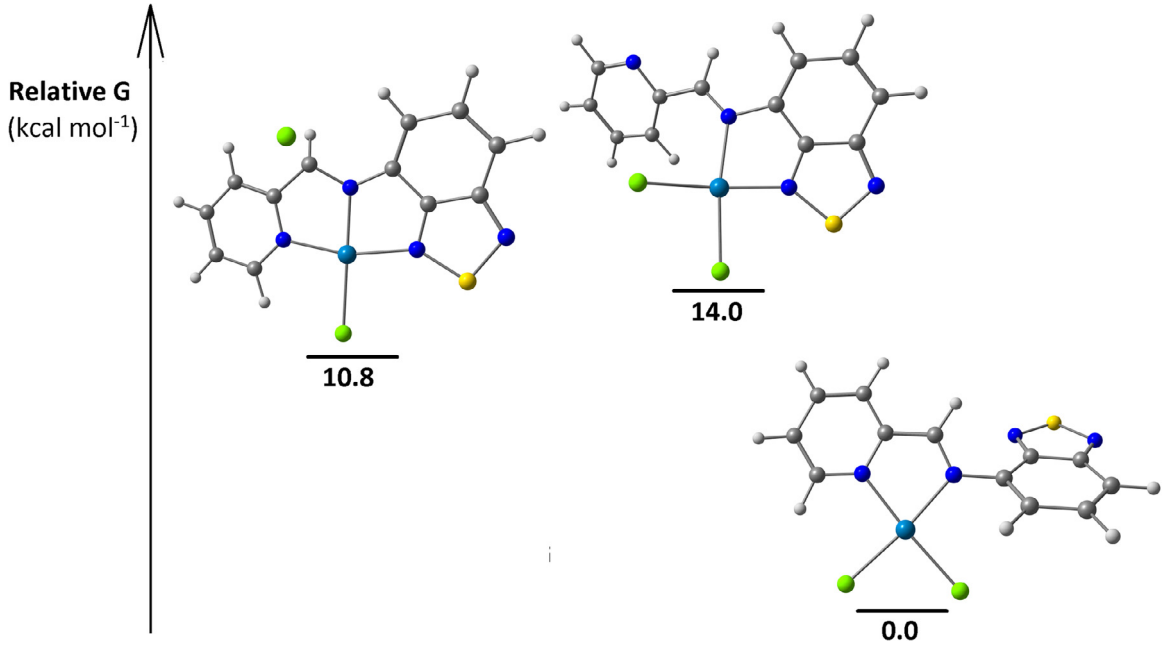


Fig. 1. DFT-optimized isomers of $[PdCl_2(pyN^{BTD})]$ (C-PCM/MN15/def2-SVP, DMSO as continuous medium) and relative Gibbs energy values (kcal mol^{-1}). Colour map: Pd, turquoise; Cl, green; S, yellow; N, blue C, grey; H, white.

Table 2
Selected bond lengths [Å] and angles [°] for $[Pd\{C(O)CH_3\}Cl(pyN^{BTD})]$.

Pd(1)-C(21)	Pd(1)-C(21)	Pd(1)-N(1)	2.0833(12)
Pd(1)-N(2)	2.2914(12)	Pd(1)-Cl(1)	2.3343(4)
N(1)-Pd(1)-N(2)	77.75(5)	C(21)-Pd(1)-Cl(1)	84.75(5)
C(21)-Pd(1)-N(1)	93.45(6)	N(2)-Pd(1)-Cl(1)	103.96(3)
N(1)-Pd(1)-Cl(1)	176.46(3)	C(21)-Pd(1)-N(2)	171.13(5)

plexes containing Schiff bases derived from pyridine-2-aldehyde the ligands show some anisobidentate behaviour, even with identical *trans* ligands. However, these differences are usually less than 0.1 Å, with the bond involving the pyridine fragment being longer than the one formed by the imine [105]. Different *trans* ligands may play a role [106,107], and the acyl ligand is known to produce a much more *trans* influence than the chloride, as was shown by Elguero *et al.* [108], justifying the different Pd-N bonds observed in $[Pd\{C(O)CH_3\}Cl(pyN^{BTD})]$.

The plane defined by the atoms Pd(1)-C(22)–C(21)–O(1) (root mean square of 0.0060 Å) makes an angle of 74.06 (6)° with the coordination plane (r.m.s. 0.0225 Å). *Trans* angles in the square planar arrangement are equal to 171.13(5) and 176.46(3)°, with the most distorted involving the chlorine atom. The chelate angle of 77.75(5)° imposes some strains on the structure, and the chlorine atom is probably interacting with the benzene ring of BTD. For these reasons, the *cis* angles involving the chlorine atom are equal to 84.75(5) and 103.96(3)°, while the third *cis* angle (C-Pd-N) is much closer to the theoretical 90°, corresponding to 93.45(6)°. The

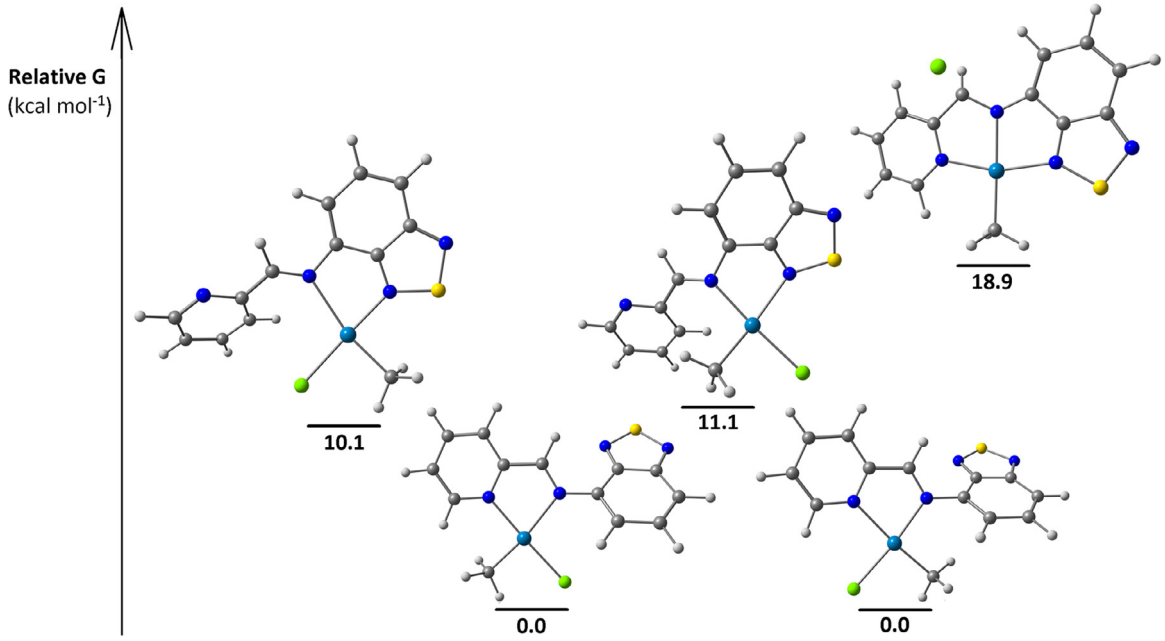


Fig. 2. DFT-optimized isomers of [Pd(CH_3)Cl(pyN^{BTD})] (C-PCM/MN15/def2-SVP, DMSO as continuous medium) and relative Gibbs energy values (kcal mol^{-1}). Colour map: Pd, turquoise; Cl, green; S, yellow; N, blue C, grey; H, white.

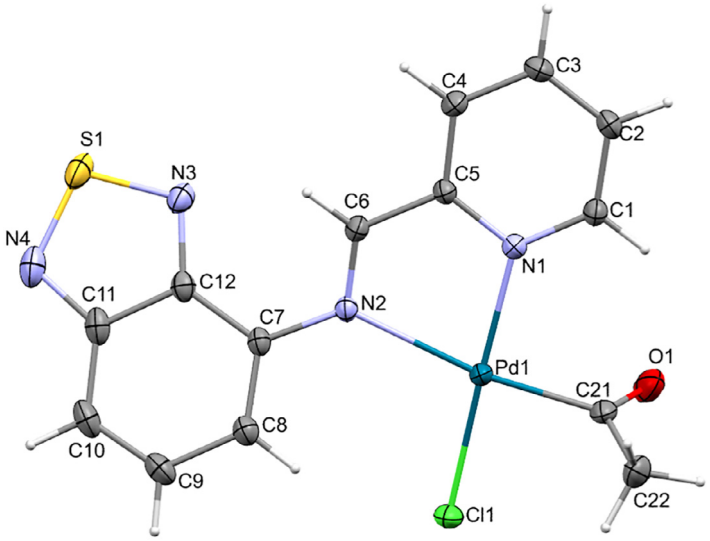


Fig. 3. X-ray structure of [Pd{$C(O)CH_3$}Cl(pyN^{BTD})].

sum of the *cis* angles amounts to 359.91°, confirming the planarity of the coordination polyhedron, with τ_4 between 0.09 [109] and 0.07 [110].

It is worth noting that [Pd{$C(O)CH_3$}Cl(pyN^{BTD})] exhibits a peculiarity related to the dihedral angle between the pyridine and the other aromatic fragment, normally defined as ϕ angle [111]. The ϕ values reported in the literature for other pyridine-2-imine complexes with an aromatic ring directly bonded to the imine group are comprised between 60 and 90°. In the case of [Pd{$C(O)CH_3$}Cl(pyN^{BTD})], this angle is 17.45(2)°, *i.e.* the rings are almost coplanar, far from the value of 63° proposed for the expected atropisomer. To the best of our knowledge, a similar situation was never observed before [112]. As expected for planar atropisomers, this disposition allows some stacking interaction between neighbour molecules, as shown in Figs. 4 and S13 (unit cell content), with Pd-$C4^{i}$ (i, 1/2-x, y-1/2, 1/2-z) and C6-$O4^{i}$ distances respectively equal to 3.1722(14) Å and 3.3344(19) Å (CHO angle = 135°, H…O distance = 2.59 Å).

DFT calculations on the possible isomers of [Pd{$C(O)CH_3$}Cl(pyN^{BTD})], either *in vacuo* and considering dichloromethane as continuous medium, confirmed that the most stable isomers are neutral species with the $N_{pyridine}$ and N_{imine} atoms bonded to the metal centre (Figures S14-S15). Moreover, the isomer with the acyl ligand *trans* to N_{imine} is more stable than the one with the acyl *trans* to $N_{pyridine}$ (about 0.6 kcal mol^{-1} with implicit solvation, 2.2 kcal mol^{-1} in the gas phase), according to the X-ray diffraction outcomes.

Following previously reported results on other palladium(II) derivatives [113–117], catalytic tests were conducted on the three pyN^{BTD} complexes for the palladium-catalysed methoxycarboxylation of iodobenzene to methyl benzoate. The complexes resulted to be active towards this reaction, and the results in terms of TON are

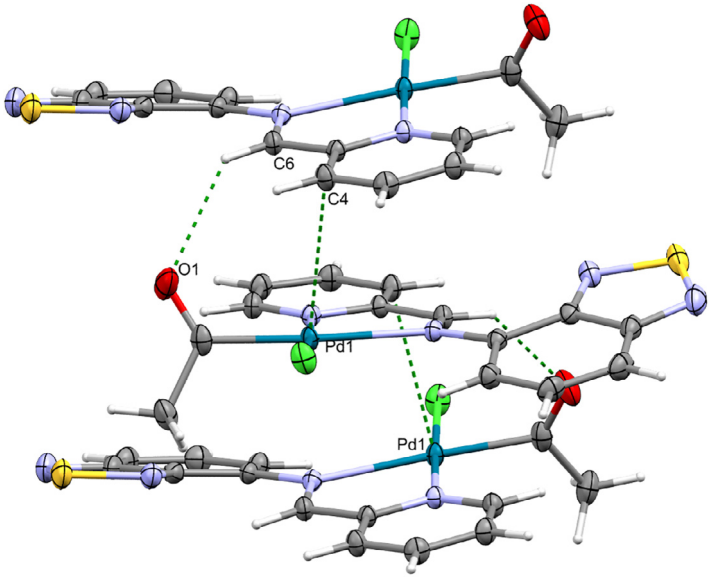
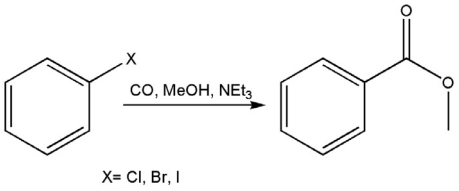


Fig. 4. Intermolecular stacking interaction in [Pd{C(O)CH$_3$}Cl(pyN^{BTD})].

Table 3
Catalytic activity towards the methoxycarboxylation reaction of halo-benzenes (Ph-X) to methyl benzoate.

Catalyst	Ph-**X**	TON	Reaction
[$PdCl_2(MeCN)_2$]	Cl	n.d.	
[$PdCl_2(MeCN)_2$]	Br	n.d.	
[$PdCl_2(MeCN)_2$] [118]	I	n.d.	
[$Pd(OAc)_2$]	Cl	n.d.	
[$Pd(OAc)_2$]	Br	12	
[$Pd(OAc)_2$]	I	194	
[$Pd(OAc)_2$(phen)]	Cl	5	
[$Pd(OAc)_2$(phen)]	Br	15	
[$Pd(OAc)_2$(phen)]	I	351	
[$PdCl_2$(pyN^{BTD})]	Cl	n.d.	
[$PdCl_2$(pyN^{BTD})]	Br	8	
[$PdCl_2$(pyN^{BTD})]	I	356	
[Pd(CH$_3$)Cl(pyN^{BTD})]	Cl	6	
[Pd(CH$_3$)Cl(pyN^{BTD})]	Br	12	
[Pd(CH$_3$)Cl(pyN^{BTD})]	I	372	
[Pd{C(O)CH$_3$}Cl(pyN^{BTD})]	Cl	8	
[Pd{C(O)CH$_3$}Cl(pyN^{BTD})]	Br	12	
[Pd{C(O)CH$_3$}Cl(pyN^{BTD})]	I	379	

summarized in Table 3, compared with [$PdCl_2(MeCN)_2$], [$Pd(OAc)_2$] and [$Pd(OAc)_2$(phen)]. The three complexes showed closely similar TON values, between 356 and 379, thus suggesting the formation of the same catalytically active species in the reaction mixture. The TON values are meaningfully higher than the one obtained with [$Pd(OAc)_2$] or [$PdCl_2(MeCN)_2$], taken as a reference [118], and are roughly comparable with that observed using another complex with a N-donor chelate in the coordination sphere as catalyst, [$Pd(OAc)_2$(phen)], under the same experimental conditions. The tests on bromobenzene and chlorobenzene led to very low yields in comparison to iodobenzene (reactivity trend: -I >> -Br > -Cl).

4. Conclusions

((Pyridin-2-yl)methylene)-4-amino-2,1,3-benzothiadiazole revealed very different coordinating features towards palladium(II) with respect to the previously reported *N*-((pyridin-2-yl)methylene)quinolin-8-amine. The ligand forms bonds with the metal centre only with the nitrogen atoms of the pyridine and imine moieties, while the 2,1,3-benzothiadiazole heterocycle remains as a free pendant with peculiar structural properties, that favour intermolecular interactions. Moreover, the metal-assisted synthesis is less straightforward, and good yields were achieved only by forming *in situ* the ligand before the interaction with the metal precursors. The differences with respect to the 8-aminoquinoline derivative appear *in primis* related to the presence of three electronegative atoms in the 2,1,3-benzothiadiazole skeleton, which reduces the nucleophilicity of the heterocycle and of the amine substituent. The study will be prosecuted considering other metal centres and functionalized five-membered N-donor heterocycles.

For what concerns the reactivity of the complexes here reported, the methyl derivative showed high reactivity towards CO, with almost immediate insertion in the Pd-C bond. All the compounds behaved as catalysts towards the methoxycarboxylation of iodobenzene, with activities is line with the presence of a bidentate π-conjugated N-donor chelating ligand in the coordination sphere.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2023.122711.

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