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Research paper

Novel κ^2 -N_{im},S- and κ^4 -C,N_{im},(μ -S),(μ -S)-coordination of di-2-thienyl ketone thiosemicarbazone (dtktsc). Hydrogen evolution and catalytic properties of palladacyclic [Pd(κ^4 -C,N_{im},(μ -S),(μ -S)-dtktsc-2H)]₄



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ABSTRACT

The reaction between di-2-thienyl ketone thiosemicarbazone, dtktsc, (1) and Zn(OAc)₂·2H₂O in ethanol produced [Zn(κ^2 -N_{im},5-dtktsc-H)₂] (2). When PdCl₂(CH₃CN)₂ was used in place Zn(OAc)₂·2H₂O novel [Pd(κ^4 -C,N_{im}, (µ-S),(µ-S)-dtktsc-2H)]₄ (3) was isolated. These reactions are in contrast with those reported for the synthesis of [Zn(κ^3 -N_{py},N_{im},S-dpktsc-H)₂] and [PdCl(κ^3 -N_{py},N_{im},S),PdCl₂(κ^2 -N_{py},N_{am})-dpktsc-H)] • CH₃CN when di-2-pyridyl ketone thiosemicarbazone (dpktsc) was used in place of 1. The identities of 2 and 3 were established from results of their elemental compositions, spectroscopic and electrochemical properties. The κ^2 -N_{im},S-coordination of the imide deprotonated dtktsc (dtktsc-H)⁻ to the Zn(II) ion was established from ¹³C and ¹H NMR measurements. X-ray structural analysis on a single crystal of 3 • dmf confirmed the κ^4 -N_{im},C,(µ-S),(µ-S)-coordination of amide deprotonated and thienyl metallated dtktsc (dtktsc '2H)²⁻ to the Pd(II) ion. In action of solutions of 2 and 3, along with electrochemical reactions of dtktsc with Zn(OAc)₂·2H₂O and PdCl₂(CH₃CN)₂ revealed facile co-ordination of dtktsc to the metal ions. The palladacyclic 3 shows good electro-catalytic behavior toward proton reduction and moderate catalytic activity toward C–C cross-coupling reactions.

1. Introduction

Thiosemicarbazones and their metal compounds continue to attract research due to their physico-chemical properties [1-7], and implications in various chemical [8-17] and biological [18-22] processes. A SciFinder search on thiosemicarbazone revealed over 11,000 research articles since 1948 and a ScienceDirect search on thiosemicarbazone found over 6,000 references that include over 3,500 research articles, and more than 400 review articles since 1996. Thiosemicarbazones were realized in the late 19th century as derivatives of ketones and aldehydes. The binding of thiosemicarbazones to wide range of metal ions via the thiolate S atom and azomethine (imine) N atom to form five-membered metallocyclic ring was realized in the early 20th century [4]. The facile acid catalyzed condensation of the carbonyl (C=O) group of various ketones or aldehydes with the amine (NH₂) group of thiosemicarbazide $[NH_2-NH-C(=S)NXY]$ (X and Y = H, alkyl or aryl) allow for the design and synthesis of broad range of compounds containing the thiosemicarbazone [C=N-NH-C(=S)-NXY] moiety (see Scheme 1).

Hydrazonic compounds that include hydrazones, semi- and thiosemicarbazones possess a range of electron donor and electron acceptor sites, making them susceptible to attack by various nucleophilic and electrophilic reagents [23,24]. This allows for the development of variety thiosemicarbazone chemosensors for the detection, and determination of trace amounts of anions [8-10], and cations [11,12,15] in environmental and biological samples. The anion-sensing behavior of thiosemicarbazones is due to hydrogen bonding between the anion and the thioamide proton [9]. Thiosemicarbazones bind to metal moieties utilizing various binding modes to form variety of mononuclear [1,2,4,13,14] and poly-nuclear [17,25,26] complexes. The antitumor, antiviral, antibacterial, antifungal and antimalarial characteristics of several thiosemicarbazones have been verified [17,18,20,27,28]. Pyridyl thiosemicarbazone derivatives such as di-2-pyridyl ketone-4,4-dimethyl-3-thiosemicarbazone (Dp-44mT) [20] and di-2-pyridyl ketone-4-cyclohexy-4-methyl-3-thiosemicarbazone (DpC) [27] are in clinical trials for the treatment of various cancers that include pancreatic carcinoma and lung cancer [6,28]. Several thiosemicarbazones along with their Gold (I) and (III) and Pd(II) complexes are effective antimalarial

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 $R_1, R_2 = H$, alkyl or aryl and X, Y = H, halide, R_1 or R_2

Scheme 1. Representation of the synthesis of thiosemicarbazones.

agents [22,28]. The excellent chelating properties of thiosemicarbazones account in part for their bioactivities and molecular sensing properties. The catalytic properties of several thiosemicarbazone complexes have been explored in processes that include C–C [13,14,17], C–N [29], C–O [30] cross-coupling reactions, H₂ evolution [21,31,32], etc.

We have been interested in the chemistry of di-2-pyridyl ketone (dpk) and di-2-thienvl ketone (dtk) and their hydrazonic derivatives that include hydrazones (dxk-h), oximes (dxk.oxime), semicarbazones (dxksc) and thiosemicarbazones (dxktsc) (x = p or t) and their metal compounds and reported on their synthesis, spectroscopic, solid state structures and molecular sensing and catalytic properties [24,25,31,33-36]. Although reports appeared on the coordination of thiosemicarbazones to metal ions in bidentate (x²-N_{py},N_{py}) [14,36], tridentate (κ^3 -N_{py},N_{im},S) [1,26,28], tetra-dentate (κ^4 -N_{py},N_{im},S,N_{py}) [13,25] and penta-dentate (κ^5 -N_{py},N_{im},N_{py},N_{am}) [24] modes (py = pyridyl, im = imine, and am = amide) there has been no report on the coordination chemistry of di-2-thienyl ketone hydrazonic compounds [33,35]. In continuation of our efforts to develop the chemistry of di-2thienyl ketone hydrazonic compounds [33,35], in this report, we describe the synthesis, spectroscopic, electrochemical and catalytic properties of the first metal compounds of dtktsc (1).

2. Experimental

2.1. Reagents

PdCl₂ and di-2-thienyl ketone (dtk) were purchased from BDH, Ltd. and Sigma-Aldrich, respectively. All other reagents were obtained from commercial sources and used without modification. Di-2-thienyl ketone thiosemicarbazone (dtktsc) (1) was prepared from the acid catalyzed condensation reaction between di-2-thienyl ketone (dtk) and thiosemicarbazide in refluxing acidified ethanol [35]. Solvents used in spectroscopic and electrochemical measurements were analytical grade. All manipulations were performed in open air, except for electrochemical measurements.

2.2. Preparation of $[Zn(\kappa^2-N_{im}S-dtktsc-H)_2]$ (2)

A mixture of Zn(OAc)₂·2H₂O (50 mg, 0.23 mmol), dtktsc (135 mg, 0.50 mmol) and EtOH (100 mL) was refluxed for 3 h. The mixture was allowed to cool to room temperature, and solvent was evaporated under a stream of air to ~ 20 mL. A yellow microcrystalline solid was filtered off, washed with cold ethanol and diethyl ether and dried; yield 120 mg (93%). Anal. Calcd. for C₂₀H₁₈N₆S₆Zn (%): C, 40.16; H, 2.70; N, 14.05. Found: C, 40.08; H, 2.90; N 13.90. Infrared data (ATR, neat/cm⁻¹): ν (N–H of NH₂) 3,325 and 3,292, ν (C–H) 3,163, and 3,089, ν (C=N) and ν (C=C) 1,591–1,425, ν (C–N) 1,280. UV–vis [λ /nm, ($\epsilon \pm 500$ /M⁻¹ cm⁻¹)] in dmso: 358 (23,300), 389 (sh, 17,300); dmf: 275 (32,000), 354 (39,600), 389, (18,800). ¹H NMR (δ ppm) in d₆-dmso: 7.87 (d, 2H, NH₂), 7.54 (d, 1H), 7.17 (d, 1H), 7.08 (t, 3H), 6.95 (d, 1H).

2.3. Preparation of $[Pd-(\kappa^4-C, N_{inv}(\mu-S), (\mu-S)-dtktsc-2H)]_4$ (3)

A mixture of PdCl₂(CH₃CN)₂ (40 mg, 0.15 mmol), dtktsc (40 mg, 0.15 mmol) in ethanol (50 mL) was stirred at room temperature in air for 3.5 h. The yellow reaction mixture changed to deep red. Solvent was evaporated away under a stream of air to 15 mL and left to stand for 2 h. A red powder was filtered off, washed with hexanes, and diethyl ether, and dried; yield 48 mg (61%). Anal. Calc. for C₂₀H₁₄N₆Pd₂S₆ (%): C, 32.3; H, 1.9; N, 11.3. Found: C, 32.4; H, 1.6; N, 11.3. Infrared (ATR, neat/cm⁻¹): ν (NH₂) 3,349, ν (C=N) 1,578, ν (C=C), 1,530, 1,506, 1,417. UV–Vis (λ /nm, $\varepsilon \pm 500/M^{-1}$ cm⁻¹): dmf: 296 (13,080), 307 sh (12,880), 347 (13,350), 492 (3,340), 515 sh (3,100); dmso: 346 (17,750), 516 (6,640), 528 (6,400) calculated.

2.4. Physical measurements

Electronic absorption spectra were recorded on an HP-8453A diode array and a Perkin-Elmer λ -19 UV/VIS/NIR spectrometer. Solution ¹H and $^{13}\mathrm{C}\,\mathrm{NMR}$ spectra were recorded on a Bruker 500 DRX spectrometer, and were referenced against the residual ¹H and ¹³C of the solvent. Infrared spectra were recorded as neat samples on a Bruker Vector 22 FT-IR spectrometer with ATR accessory. Electrochemical measurements were performed with either a Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat and Model 276 interface in conjunction with a 286 PC and the EG&G PARC Headstart program or a DigiIvy DY2312 potentiostat (and software), and manipulated using Microsoft Excel, under an argon atmosphere at room temperature. Ferrocene, which was used as an internal reference showed a reversible wave at +0.65 V. Measurements were performed on solutions that were 0.1 M in [^{*n*}Bu₄N]PF₆. The $E_{p,a}$, $E_{p,c}$ and $E_p = (E_{p,a} + E_{p,c})/2$ values were referenced to Ag wire quasi-reference electrode at room temperature and are uncorrected for junction potentials. The number of electrons on the redox waves was determined using the oxidative peak current of the reversible one-electron couple of FeCp2/FeCp2+ as an internal standard. Electrochemical cells were of conventional design based on scintillation vials or H-cells. A glassy-carbon and a Pt-wire were used as the working and counter electrodes, respectively.

2.5. X-ray crystallography

Crystals of $[Pd(\kappa^4-C, N_{im}, (\mu-S), (\mu-S)-dtktsc-2H)]_4 \cdot dmf$ (**3.dmf**) were grown from a dmf solution of **3** when left to stand at room temperature in air for several days. A single crystal was selected, mounted on a glass fiber and placed in the goniometer. A Bruker SMART APEX CCD areadetector diffractometer equipped with Mo-Kα radiation and a graphite monochromator was used for data collection. The Bruker (2009) SAINT was used for cell refinement and data reduction and the multi-scan absorption correction was implemented using SADABS [37,38]. SHELXL-2018/3 was used for structure analysis [39]. All hydrogen atoms were assigned by assuming idealized geometries with $d_{(C-H)} = 0.93$, 0.96 for aromatic and aliphatic, respectively and $d_{(N-H)}$ = 0.86 Å with U_{iso} (H) = 1.2 U_{eq} (N) and Uiso(H) = 1.5 Ueq(C). All nonhydrogen atoms were refined anisotropically. In the final refinement, a

Table 1

C	rystal	Ċ	lata	and	structure	refinement	for	mono2.
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Identification code	$-3 \cdot dmf$
Empirical formula	C ₂₃ H ₁₇ N ₇ OPd ₂ S ₆
Formula weight	812.60
Temperature	301(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, Cc/2
Unit cell dimensions	$a = 26.734(2) \text{ Å } \alpha = 90^{\circ}$
b = 15.2701(13) Å	$\beta = 133.429(2)^{\circ}$
c = 19.1945(17) Å	$\gamma = 90^{\circ}$
Volume	5690.6(9) Å ³
Z, Calculated density	8, 1.897 Mg/m ³
Absorption coefficient	1.737 mm^{-1}
F(0 0 0)	3200
Crystal size	0.49 \times 0.37 \times 0.27 mm
θ range for data collection	2.92 to 28.37°
Limiting indices	$-35 \le h \le 35, -20 \le k \le 20, -25 \le l \le 25$
Reflections collected / unique	75,714 / 7096 [R(int) = 0.0563]
Completeness to theta $= 28.37$	99.4%
Max. and min. transmission	0.6513 and 0.4832
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	7096/0/353
Goodness-of-fit on F ²	1.106
Final R indices [I greater than 2σ (I)]	R1 = 0.0801, wR2 = 0.1440
R indices (all data)	R1 = 0.1238, wR2 = 0.1600
Extinction coefficient	0.00025(3)
Largest diff. peak and hole	2.057 and −0.861 e.Å ⁻³
CSD #	1,980,792

region of electron density (2.14 e·Å⁻³) at 0.63 Å from C35 points to the potential partial charge on the complex due to thione-thiol tautomerization during crystallization. Table 1 shows cell parameters and other

crystallographic information.

2.6. C-C cross coupling reactions

A mixture of **3** (1.9 µmol), phenyl boronic acid (74 mg, 0.61 mmol), anhydrous K_2CO_3 (225 mg, 1.63 mmol), aryl halide (0.38 mmol) and ethanol was added to a pressure tube, the mixture was purged with N_2 and allowed to refluxed for 6 h. The reaction mixture was left to cool to room temperature, and filtered to remove the catalyst. The filtrate was passed through a silica column that was eluted with hexanes/ethyl acetate in a ratio of 3:1. The C–C coupled products was isolated from the slow evaporation of the solvent from the eluted fractions. The resulting C–C cross coupling products were identified from the results of their ¹H and ¹³C NMR spectra.

2.7. Electro-catalytic hydrogen evolution

Controlled-potential electrolysis (CPE) measurements for the production of hydrogen were conducted at -0.7 V (vs Ag), on unstirred solutions of **3** for 17 min. A sealed two-chambered H-cell separated by a fine frit was employed for electrolysis. One chamber held the working and reference electrodes in 10 mL of 0.15 mM of complex in 0.1 M [^{*n*}Bu₄N]PF₆ (supporting electrolyte) with 11.6 mM *p*-toluenesulfonic acid monohydrate (*p*-TSOH) (proton source) and the second chamber held the auxiliary electrode in 5 mL of the solvent with the supporting electrolyte. A glassy carbon plate (contact area \sim 2 cm \times 1 cm \times 3 mm), a Pt wire and an Ag wire were used as the working, auxiliary and reference electrodes, respectively. The electrochemical cell was purged with Ar for 20 min., sealed under an Ar atmosphere during electrolysis. The amount of H₂ evolved was calculated



Scheme 2. Representation of the reactions of 1 with Zn(OAc)₂·2H₂O and PdCl₂(CH₃CN)₂.

from the charge difference in the presence and absence of the catalyst during CPE [31]. After electrolysis, 50 μ L of the headspace was injected into the gas chromatograph (GC). GC experiments were performed on an HP (Agilent) 5890 series II instrument with an ECD detector (40 °C isothermal; 1.0 mL min⁻¹ flow rate; He carrier gas) [24]. The remainder of the headspace was analyzed with a PGas-22 H₂ gas detector.

2.8. Analytical procedures

Elemental microanalyses were performed by MEDAC Ltd., Department of Chemistry, Brunel University, Uxbridge, United Kingdom.

3. Results and discussion

3.1. Synthesis and characterization

Di-2-thienyl ketone thiosemicarbazone (1) reacts with Zn $(OAc)_2$ ·2H₂O in refluxing ethanol and with PdCl₂(CH₃CN)₂ at room temperature to form $[Zn(\kappa^2-N_{im},S-dtktsc-H)_2]$ (2) and $[Pd(\kappa^4-C,N_{im},(\mu-S),(\mu-S)-dtktsc-2H)]_4$ (3), respectively (see Scheme 2). Complexes 2 and 3 are the first examples of metal compounds of 1. The identities of 2 and 3 were established from the results of their elemental composition, and spectroscopic, and electrochemical properties. The authenticity of 3 was confirmed from X-ray crystallographic analysis done on a single crystal of 3 • dmf.

The theoretical and experimental values of the elemental composition of **2** and **3** (see experimental section) are consistent with their formulations. The infrared spectra of **2** and **3** show peaks due to ν (NH₂) and ν (C–H) between 3,500 and 2,900 cm⁻¹, combined ν (C=N) and ν (C=C) between 1,600 and 1,400 cm⁻¹, δ (C–H), ν (C–N) and ν (C–C) between 1,400 and 1,000 cm⁻¹, ν (C–S) between 1,000 and 800 cm⁻¹ and δ (C–H and N–H) < 800 cm⁻¹ consistent with their formulations. A comparison of these spectra with the spectrum of **1** (see Supplementary Fig. S1) show changes in the combined ν (C=N) and ν (C=C) and ν (C–S) regions consistent with the thiol κ^2 -N_{im},S-

coordination of **1**.

 ^{13}C NMR and ^{1}H NMR measurements in dmso-d_6 and dmf-d_7 (see Table S3 and experimental section) confirmed the identity of 2. ¹³C NMR spectrum of 2 shows ten carbon resonances, and the ¹H NMR spectrum shows six proton resonances in the aromatic region. These results hint to non-equivalent thienyl rings. A single resonance appeared for the two amine protons (NH₂) in the ¹H NMR spectrum showing that the NH₂ protons are equivalent. Fig. 1 shows the ¹H NMR spectra of 1 and 2 measured in dmso-d₆ and dmf-d₇. These spectra show the disappearance of the amide NH proton consistent with the thiolate coordination of the amide deprotonated dtktsc (dtktsc-H)⁻ to Zn(II). The amine protons of 2 coalesce and significantly shift upfield compared to the non-equivalent amine protons of 1. The aromatic protons of 2slightly shift upfield compared the aromatic protons of 1. Further, in dmf-d₇, the aromatic and amine protons shift downfield compared to dmso-d₆ pointing to stronger interaction between dmf-d₇ and the metal complex.

Variable temperature ¹H NMR measurements in dmso-d₆ (see Fig. 2) and dmf -d₇ (see Supplementary Fig. S2) show the amine protons shift significantly upfield as the temperature increases. In dmso-d₆, H23 slightly shifts down field and in dmf-d₇, H11 and H21 slight shift upfield as the temperature increases. Integration of H11 and the amine (NH₂) protons gave a ratio of 1:2 at all temperature pointing to non-exchangeable amine protons. The residual water protons in both solvents shift upfield as the temperature increased. These results point to a plausible hydrogen bonding between the amine protons and the residual water molecules in the solvent.

The identity of **3** was confirmed from X-ray structural analysis done on a single crystal grown from dmf solution of **3**. Views of the asymmetric unit, and molecular structure of $[Pd(\kappa^4-C,N_{im},(\mu-S),(\mu-S)-dtktsc 2H)]_4 \cdot dmf ($ **3**· dmf) are shown in Fig. 3. The asymmetric unit (Fig. 3a) $contains well separated <math>[Pd(\kappa^3-C,N_{im},S-dtktsc-2H)][Pd(\kappa^4-C,N_{im},S,(\mu-S)-dtktsc-2H)]$ and a dmf molecule. The dinuclear $[Pd(\kappa^3-N,S,C-dtktsc 2H)][Pd(\kappa^4-S,C,N_{im},(\mu-S)-dtktsc-2H)]$ units are linked via the thiolate S atom of $[Pd(\kappa^3-C,N_{im},S-dtktsc-2H)]$. The non-coordinated S atom of $[Pd(\kappa^4-C,N_{im},S,(\mu-S)-dtktsc-2H)]$ remains exposed for potential



Fig. 1. ¹H NMR spectra measured at 298 K of (a) 1 in dmso-d₆, (b) 2 in dmso-d₆, (c) 1 in dmf-d₇, and (d) 2 in dmf-d₇.



Fig. 2. Variable temperature ¹H NMR spectra of 2 measured in dmso-d₆.

coordination to other atom. This was confirmed when the molecular structure was developed (Fig. 3b). The ligating atoms of **3** are a thienyl C atom, an imine N atom, a thiolate S atom of $(dtktsc-2H)^{2-}$, and the bridging thiolate S atom of adjacent [Pd(κ^3 -C,N_{im},S-dtktsc-2H)]. The coordination geometry around Pd(II) in 3 is approximately square planar (see Fig. 3c). Deviation from idealized square planar geometry is due to κ^3 -C,N,S-coordination of (dtktsc-2H)²⁻ to the Pd(II) ion. This is evident from C13-Pd1-N1 and N1-Pd1-S3 bite angles of 81.2(3) and 82.59(19)°, respectively. The trans angles Cl3-Pd1-S3 and N1-Pd1-S6 of 162.7(3) and 175.61(19) bent away from the idealized 180° of square planar geometry. The bond distances and angles of **3** • **dmf** are normal and similar to those reported for closely related compounds (see Table S1) [14,17,21,24,40,41]. The extended structure of 3 • dmf (see Supplemental Fig. S3) shows stacks of $[Pd(\kappa^4-C,N_{im},(\mu-S),(\mu-S),dtktsc-2H)]_4$ · dmf units linked via a network of intra- and intermolecular hydrogen bonds (see Table S2).

The electronic absorption spectra of **2** measured in protophilic solvents (dmf or dmso) show high sensitivity to their surroundings. Fig. 4 shows the electronic absorption spectra of **2** and **1** measured in dmf in the presence and absence of acetic acid (HOAc) and sodium acetate (NaOAc). These spectra show **2** to dissociate in the presence of HOAc and NaOAc to form $Zn(OAc)_2$, dtktsc and (dtktsc-H)⁻. The electronic transition observed in the presence of excess acid at 350 nm is due to dtktsc and the electronic transition at 430 nm is due to (dtktsc-H)⁻. The electronic transitions of **2** shift to low energy compared to the electronic transitions of **1**. This is due to the coordination of the electron rich (dtktsc-H)⁻ to the electron rich Zn(II) ion. The electronic transitions of **2** are ILCT due to $\pi \rightarrow \pi^*$ of the imine (C=N) of the hydrazonic backbone followed by charge transfer to the thienyl ring or vice versa. The



Fig. 3. Views of (a) the asymmetric unit, (b) molecular structure, and (c) coordinated atoms of 3·dmf.

appearance of a shoulder at 393 nm in close proximity to the transition at 373 nm hints that the coordinated (dtktsc-H)⁻ anions are not equivalent. Spectrophotometric titration of dmf solution of **1** with stoichiometric amounts of Zn(OAc)₂·2H₂O confirmed the facile coordination of **1** to Zn(II) ion (see Supplementary Fig. S4).

The electronic absorption spectra of 3 measured in dmf and dmso (see supplementary Fig. S5) show a broad electronic transition between 600 and 400 nm, along with an intra ligand charge transfer (ILCT) transition at 353 nm, and $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transitions of the hydrazonic moiety at 315 and 293 nm. The board character of the low energy electronic transition points to charge-transfer, and is assigned to ${}^{1}A_{1g} \rightarrow {}^{1}E_{g}$, ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$ and ${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$ of d⁸ electronic configuration of Pd(II) mixed with metal-to-ligand charge-transfer (MLCT), ligand-to-metal charge-transfer (LMTC) and intra ligand charge-transfer (ILCT). This is similar to the spectra reported for variety of Pd(II) complexes of Schiff bases and hydrazonic compounds that include [PdCl(κ^3 -N_{py},N_{im},O-dpk-h)] (dpkbh = di-2-pyridyl ketone benzoyl hydrazone and dpk4abh = di-2-pyridyl ketone 4-amino benzoyl hydrazone) [31] and [Pd₂Cl₃(κ⁵-N_{py},N_{im},S,N_{py},N_{am}-dpktsc-H)] [35] (see Fig. S5). The *d*-*d* electronic transitions of **3** are red shifted compared to the electronic transitions of other Pd(II)-complexes due to



Fig. 4. Electronic absorption spectra measured in dmso of (a) 2, $6.00x10^{-6}$ M; (b) 2 + NaOAc, $1.00x10^{-5}$ M; (c) 2 + HOAc, $1.00x10^{-5}$ M; (c) 1, $8.20x10^{-6}$ M and (d) 1 + NaOAc, $1.00x10^{-5}$ M. M.

the electron donating character of $(dtktsc-2H)^{2-}$. In dmf, the *d-d* transitions of **3** appeared at 523, 490 and 470 nm, and in dmso at 546, 517 and 482. The ILCT electronic transition at 353 nm appeared at the same energy as the ILCT transition of dtktsc confirming the coordination of the ligand to Pd(II) ion. The *d-d* electronic transitions of [PdCl(κ^{3-} N_{py},N_{im},O-dpkbh)] appeared at 445 nm with shoulders at 470 and 415 nm in dmso or dmf [31]. The $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of **3** shift to low energy compared to the electronic transitions of dtktsc.

The electrochemical properties of 2 and 3 measured in dmf were investigated using voltammetric techniques. Fig. 5 shows cyclic voltammograms of 1, 2, and 3 measured on reductively and oxidatively initiated scans. Cyclic voltammogram of 2 on reductively initiated scan (see Fig. 5c) shows irreversible reductions at $E_{p,c} = -1.58$, -1.90 and -2.47 V. On scan reversal at -2.80 V, electrochemically generated product waves appeared at $E_{p,a} = +0.15$ and +0.60 V along with irreversible multi-electron oxidations at $E_{p,a} = +1.25$ and +1.50 V. Square wave voltammograms measured between 0 and -2.5 V and 0.00 to + 2.00 V (see Supplemental Figure S6) show peaks at -1.53, -1.62, -1.79, -2.19, -2.30, +1.10, and + 1.28 V. The voltamogram of 1 measured under similar conditions (see Fig. 5a) shows irreversible reductions at $E_{p,c} = -1.50$, -2.00, and -2.30 V followed by electrochemically generated product waves at $E_{p,a} = +0.34$, +0.68 V and a broad multi-electron irreversible oxidations at $E_{p,a} = +1.48$ V. The first irreversible reduction wave of 1 was assigned to the imine (C=N) one electron reduction to imine radical anion (C-N)⁻. The voltammogram of Zn(OAc)₂·2H₂O measured under the same conditions shows the $Zn^{2+} \rightarrow Zn^0$ reduction wave at -1.70 V (see Supplemental Fig. S7). These results show that the reduction potentials of coordinated (dtktsc-H)⁻ shift more negative compared to dtktsc due the increase in its electron density [35]. The overlap of the redox potentials between -1.35 and -2.20 V in the voltammograms of 2 hints to mixed



Fig. 5. Cyclic voltammograms on glassy carbon working (dia = 3.0 mm) vs Ag of 1, 2 and 3.Supporting electrolyte = $0.1 \text{ M} [^{n}\text{Bu}_4\text{N}]\text{PF}_6$, scan rate 2000 mVs⁻¹.

ligand-metal reductions. This is consistent with the close proximity of the first electron reduction of **1** and the $Zn^{2+} \rightarrow Zn^0$ reduction of Zn^{2+} ion. The appearance of two peaks in the imine region in the square wave voltammogram of 2 hints that the coordinated (dtktsc-H)⁻ anions are not equivalent (see Supplementary Fig. S6). These observations are consistent with the electronic absorption and ¹H NMR measurements. On oxidatively initiated scan (see Fig. 5d), the reductively generated productive waves disappeared, and an oxidatively generated product wave appeared at -0.69 V. The results of these voltammograms disclosed oxidative and reductive decomposition of 2. Cyclic voltammograms of 2 in the presence of stoichiometric amounts of p-TSOH revealed electrochemical decomposition of 2. This is evident from the appearance of $Zn^0 \rightarrow Zn^{2+}$ stripping wave at $E_{p,a} = -0.80$ V along with a proton-coupled reduction wave observed at the same potential $(E_{p,c} = -1.70 \text{ V})$ as that observed for the electrochemical reduction of dtktsc in the presence of p-TSOH (see Supplementary Fig. S8) [35].

Voltammetric (cyclic and square wave techniques) titrations of dtktsc in dmf with stoichiometric amounts of $Zn(OAc)_2 \cdot 2H_2O$ show changes consistent with the coordination of (dtktsc-H)⁻ to Zn(II) (see Supplemental Fig. S9). When 1.38 mM Zn(OAc)_2 \cdot 2H_2O was added to an electrochemical cell containing 12.5 mM dtktsc in dmf, an irreversible reduction wave assigned to $Zn^{2+} \rightarrow Zn^0$ appeared at $E_{p,c} = -1.72$ V on reductively initiated scan (see Supplementary Fig. S9). The imine (C= N) reduction wave and oxidation waves of dtktsc were insignificantly affected by the addition of 1.38 mM Zn(OAc)_2 \cdot 2H_2O. The reduction wave of dtktsc observed at $E_{p,c} = -2.03$ disappeared and the intensity of the reduction wave at $E_{p,c} = -2.39$ V decreased upon addition of Zn (OAc)_2 \cdot 2H_2O. These results confirmed the assigned redox potentials of **2**. As the concentration of Zn(OAc)_2 • 2H_2O increased (see Supplemental Fig. S9), the imine reduction wave and Zn(II) reduction wave slightly shift more negative, and the intensity of the reduction wave at the intensity of the reduction wave and the intensity of the reduction for $Zn(OAc)_2 \cdot 2H_2O$ increased (see Supplemental Fig. S9), the imine reduction wave and Zn(II) reduction wave slightly shift more negative, and the intensity of the reduction wave at the intensity of the reduction wave at the intensity of the reduction wave and Zn(II) reduction wave slightly shift more negative, and the intensity of the reduction wave at t

Table 2

Homogeneous catalysis (Suzuki-Miyaura C-C cross-coupling).

$Br + B(OH)_2 \xrightarrow{EtOH, K_2CO_3} $								
Entry	Pre-catalyst	% Yield ^a	Refs.					
1	$[PdCl_2(\kappa^3-N_{pv},N_{im},O-dpk4abh)]$	87	[31]					
2	$[PdCl_2(\kappa^3 - N_{pv}, N_{im}, O - dpkbh)]$	88	[31]					
3	[Pd ₂ Cl ₃ (κ^5 -N _{nv} ,N _{im} ,S,N _{nv} ,N _{am} -dpktsc-	15	[31]					
	H)]							
4	$[Pd(\kappa^4-C,N_{im},(\mu-S)(\mu-S)dtktsc-2H)]_4$	8	This work					
5	[PdCl(pdcta)]	78	[42]					
6	[PdCl(pbcta)].HCl	61	[42]					

^a Isolated yields, an average of two runs.

-2.39 V significantly decreased. The intensity of the reductively generated product waves of dtktsc observed at + 0.34 and + 0.78 V decreased as the concentration of $Zn(OAc)_2 \cdot 2H_2O$ increased. The multielectronic oxidation of dtktsc shifted more positively as the concentration of $Zn(OAc)_2 \cdot 2H_2O$ increased. Square wave voltammetric titration of dtktsc with stoichiometric amounts of $Zn(OAc)_2 \cdot 2H_2O$ (see Supplementary Fig. S9) confirmed the coordination of (dtktsc-H)⁻ to Zn (II) ion.

Cyclic voltammogram of 3 on reductively initiated scan (see Fig. 5e) shows irreversible reductions, one electron each, at $E_{p,c} = -0.56, -1.18$, -1.45, -1.68 V and multi-electron reduction at -2.15 V. On scan reversal at -2.5 V, irreversible oxidations appeared at $E_{p,a} = +1.00$ V, +1.20, +1.30 and + 1.50 V. An oxidatively generated product wave appeared at -0.62 V on oxidatively initiated scan (see Fig. 5f). Square wave voltammograms measured between 0.00 and -2.50 V and 0.00 to + 2.00 V show peaks at -0.50, -1.15, -1.38, -1.60, -2.10, +0.98, +1.14, +1.22 and + 1.46 V. Cyclic voltammogram of equi-molar (15 mM) amounts of dtktsc and [PdCl2(CH3CN)2] in dmf (see supplementary Fig. S10) shows electrochemical behavior similar to that of 3. These results show facile coordination of dtktsc to Pd(II) and 3 is relatively stable to electrochemical reduction. On an oxidatively initiated scan, several oxidations appeared between $E_{p,a} = +0.80$ and + 1.70 V. On scan reversal, similar features as observed on reductively initiated scan, along with an electrochemically generated product wave appeared in the vicinity of $Pd^{2+} \rightarrow Pd^+$ reduction. The electrochemically generated product wave is due to the catalytic reduction of protons generated from the oxidation of the imine and residual water in the solvent [35].

3.2. Catalytic properties of $[Pd(\kappa^4-C, N_{inv}(\mu-S), (\mu-S)-dtktsc-2H)]_4$ (3)

The catalytic behavior of **3** toward proton reduction and C-C cross coupling reactions were investigated following the same procedures reported for catalytic behavior of Pd(II)-complexes of di-2-pyridyl ketone hydrazonic compounds and N,S-pincer type systems [24,31,42]. Cyclic voltammograms of 3 in the absence and presence of stoichiometric amounts of p-TSOH are shown in Supplementary Fig. S11. The voltammograms in the presence of p-TSOH show current enhancement at the first reduction wave, and electrochemically generated product waves at $E_{\rm p,a}$ = -0.27 V and $E_{\rm p,c}$ = + 0.30 V due to oxidation and reduction of Pd⁰ and Pd²⁺, respectively. The voltammograms are similar to those reported for the electro-catalytic hydrogen evolution using other Pd(II)-hydrazonic systems [31]. A controlled potential electrolysis (CPE) experiment on 3 at -0.70 V versus Ag, when corrected for a catalyst-free solution under the same potential produced a net charge of 0.472C after 1000 s of electrolysis, with accompanying net H₂ gas of 0.026 mL and a 43% Faradaic efficiency. The overpotential associated with the catalysed proton reductions was calculated to be 290 mV[§]. The Faradaic efficiency of this system is similar to those reported for [PdCl₂(κ^3 -N_{py},N_{im},O-dpkbh)] and PdCl₂(κ^3 -N_{py},N_{im},O-dpk-4-abh)] in dmf [31].

 $[Pd(\kappa^4-C,N_{ims})(\mu-S),(\mu-S)-dtktsc-2H)]_4$ performed poorly compared to other Pd-systems of di-2-pyridyl ketone hydrazonic compounds and S,*N*-type pincer systems when tested toward C–C cross coupling reactions (Table 2) [31,42]. This is partly due to the low solubility and polymeric nature of **3**.

4. Conclusion

 $[Zn(\kappa^2-N_{im},S-dtktsc-H)_2]$ (2) and $[Pd(\kappa^4-C,N_{im},(\mu-S),(\mu-S)-dtktsc-2H)]_4$ (3) mark the first examples of metal complexes of dtktsc (1). Elemental analysis, and spectroscopic and electrochemical measurements established the identities of 2 and 3 and show facile coordination of dtktsc to Zn(II) and Pd(II) cations. X-ray crystallographic analysis done on a single crystal of $3 \cdot \text{emf}$ confirmed the identity of the palladacyclic complex. While $[Zn((\kappa^2-N_{im},S-dtktsc-H)_2]$ dissociates in acidic, basic media and redox processes, $[Pd(\kappa^4-C,N_{im},(\mu-S),(\mu-S)-dtktsc-2H)]_4$ is stable under the same conditions. $[Pd(\kappa^4-C,N_{im},(\mu-S),(\mu-S)-dtktsc-2H)]_4$ shows good electro-catalytic behavior toward proton reduction and moderate activity toward C–C cross-coupling reactions.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2020.119592.

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 $^{{}^{\$} \}eta_{\text{cat/2}} = E^{\circ}_{H^+} - 0.059 \times (pK_a) - -E_{\text{cat/2}}$.where $\eta_{\text{cat/2}}$ is overpotential at the catalytic half-wave potential, E°_{HA} (-0.92 V vs Fc⁺/Fc) is the reduction potential of *p*-TSOH and, pK_a of *p*-TSOH (2.6) in DMF and $E_{\text{cat/2}}$ is determined from Pd^{II/I} in the presence *p*-TSOH *vs* Fc⁺/Fc using square wave voltammetry.

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