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Novel binuclear palladium(II) complexes of 2-oxoquinoline-3-carbaldehyde Schiff bases: Synthesis, structure and catalytic applications

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ABSTRACT

A series of novel binuclear Pd(II) complexes of the type $[(PPh_3)_2ClPd(L)PdCl]$ [where L = dianionic bridged ligands derived from 2-oxo-1,2-dihydroquinoline-3-carbaldehyde or its derivatives with *o*-aminophenol/*o*-aminothiophenol] have been reported. The new complexes have been characterized by elemental analysis, FT-IR, UV–Vis and NMR (^{1}H and ^{31}P) spectroscopic techniques. The coordination mode of the ligands and the geometry of the complexes were confirmed by single crystal X-ray crystallography of one of the complexes. The catalytic efficiency of one of the binuclear Pd(II) complexes was tested for N-arylation of imidazole.

1. Introduction

Heterocyclic compounds containing nitrogen atom attract a great deal of attention in coordination chemistry and homogeneous catalysis [1–3]. The combination of heterocyclic ring and azomethine moiety exerts potential biological and catalytic activities [4–6]. Although extensive studies have been made on the transition metal complexes of various nitrogen heterocyclic Schiff base ligands, comparatively less is reported on transition metal complexes derived from 2-oxo-1,2-dihydroquinoline-3-carbaldehyde [7–9]. The incorporation of phosphine ligands into the platinum group metal complexes brings remarkable changes in structural and electronic rearrangements, chemical reactivity and physical properties because of their large steric demands as well as σ-donor and π-acceptor properties [10].

Metal-catalyzed Ullmann-type C–N coupling reaction represents one of the most efficient methods to form various C–N bond containing compounds that have important biological, pharmaceutical, or material properties [11]. Traditional Cu-catalyzed Ullmann reactions require the use of stoichiometric amounts of copper, harsh reaction conditions, strong bases and often use of toxic polar solvents such as hexamethylphosphoramide (HMPA), and thus limited their large scale applications in industries. One of the most significant achievements in this field is the development of palladium-catalyzed cross-coupling reactions that became a major synthetic protocol for the construction of aryl–carbon bonds [12]. The palladium-catalyzed cross-coupling reactions may also be applied to the formation of C–heteroatom such as C–N, C–O, C–S bonds [13]. On the other hand, Buchwald–Hartwig amination has been widely used for the preparation of aryl amines by the reactions of aryl halides with primary or secondary amines, amides, sulfonamides, imines, and heterocyclic compounds containing N–H bonds [14]. N-arylation reactions catalyzed by the palladium complexes are performed under mild conditions [15]. Though many reports are available on the palladium complexes as catalysts for C–N cross coupling reactions [16–18], palladium(II) complexes containing triphenylphosphine as well as Schiff base are rarely explored. So herein, we report the synthesis and characterization of novel binuclear Pd(II) complexes containing Schiff base ligands derived from 2-oxo-1,2-dihydroquinoline-3-carbaldehyde or its derivatives and *o*-aminophenol/*o*-aminothiophenol. The novel binuclear Pd(II) complexes have been tested as catalysts for N-arylation of imidazole. The general structure of quinoline based Schiff base ligands is given in Fig. 1.

2. Experimental

2.1. Materials

All the reagents were purchased from Merck or Sigma–Aldrich and used as received. Solvents were freshly distilled and dried over the appropriate drying agents. 2-Oxo-1,2-dihydroquinoline-3-carbaldehyde, its derivatives or 2-oxo-1,2-dihydrobenzo[h]quinoline-3-carbaldehyde and the starting complex $[PdCl_2(PPh_3)_2]$ were prepared according to the reported literature procedures [19–21].

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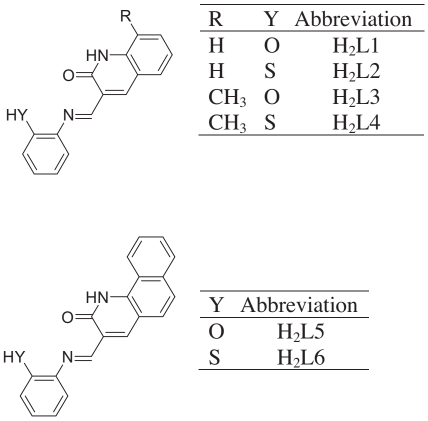

R	Y	Abbreviation
H	O	H_2L1
H	S	H_2L2
CH_3	O	H_2L3
CH_3	S	H_2L4

Y	Abbreviation
O	H_2L5
S	H_2L6

Fig. 1. Structure of quinoline based Schiff base ligands.

2.2. Physical measurements

IR spectra of the ligands and complexes were recorded on a Nicolet FT-IR spectrophotometer using KBr pellets. Electronic spectra of the complexes were recorded in dichloromethane using Systronics 119 spectrophotometer in the 200–800 nm range. Magnetic susceptibility measurements were made with the EG & G-Parc vibrating sample magnetometer. Nuclear Magnetic Resonance spectra were recorded on Bruker Avance 500 MHz spectrometer. ^{1}H NMR chemical shifts were reported using tetramethylsilane (TMS) as the internal standard. ^{31}P NMR spectra were measured relative to H_3PO_4 as the external standard. Elemental analysis of the complexes was performed by Vario EL III elemental analyser. Melting points were determined with Raaga melting point apparatus.

2.3. General preparation of 2-oxo-1,2-dihydroquinoline-3-carbaldehyde or 2-oxo-1,2-dihydrobenzo[h]quinoline-3-carbaldehyde Schiff bases

A methanol (20 cm^3) solution of either *o*-aminophenol or *o*-aminothiophenol (0.44/0.50 g; 4.00 mmol) was added to 2-oxo-1, 2-dihydroquinoline-3-carbaldehyde or its derivatives or 2-oxo-1,2-dihydrobenzo[h]quinoline-3-carbaldehyde (4.00 mmol) dissolved in the same solvent (20 cm^3) and refluxed for 6 h. The yellow precipitate that separated out was filtered and washed with methanol and dried *in vacuo*. Yield: 73–77%.

2.4. Preparation of binuclear Pd(II) complexes of the type $[(PPh_3)_2ClPd(L1)PdCl]$ (L = binucleating 2-oxoquinoline-3-carbaldehyde Schiff base ligand)

To a solution of $[PdCl_2(PPh_3)_2]$ (0.14 g; 0.20 mmol) in dichloromethane (20 cm^3), the appropriate quinoline Schiff base ligands (0.10 mmol) in methanol (25 cm^3) and two drops of triethylamine were added. The mixture was refluxed for 5 h. An orange colored precipitate that formed was separated from the solution by suction filtration. The complex was washed with ethanol and dried under *vacuum*. Yield: 66–72%.

2.5. X-ray crystallography

Crystals of $[(PPh_3)_2ClPd(L1)PdCl]\cdot 1.5CH_3CN$ suitable for X-ray diffraction study were grown from dichloromethane/acetonitrile solution. A red block crystal having approximate dimensions of 0.20 × 0.10 × 0.04 mm was mounted on a Rigaku Mercury CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71070 Å). The structure was solved by direct methods and expanded using Fourier techniques [22,23]. All non-hydrogen atoms were refined anisotropically, using full-matrix least squares refinements on F^2 with crystal structure crystallographic software package [24]. Table 1 gives further details of data collection, refinement, and the structural details of $[(PPh_3)_2ClPd(L1)PdCl]\cdot 1.5CH_3CN$.

Table 1
Crystal data and structure refinement parameters for $[(PPh_3)_2ClPd(L1)PdCl]\cdot 1.5CH_3CN$.

Empirical formula	$C_{55}H_{44.50}N_{3.50}O_2P_2Pd_2Cl_2$
Formula weight	1132.13
Color	red
Habit	black
Crystal dimensions (mm)	0.20 × 0.10 × 0.04
Wavelength (Å)	0.71070
Crystal system	orthorhombic
Lattice type	primitive
Space group	$Pna2_1$(#33)
Detector position (mm)	44.92
Pixel size (mm)	0.137
Lattice parameters	
a (Å)	16.8400(10)
b (Å)	27.7902(18)
c (Å)	10.4866(8)
V (Å^3)	4907.6(6)
Z	4
D_{calc} (g/cm^3)	1.532
F(000)	2284
μ(Mo Kα) (cm^{-1})	9.532
Absorption correction	Lorentz-polarization
Refinement method	full-matrix least squares on F^2
No. of reflections measured	total: 37292, unique: 5935
R_{int}	0.062
Reflection/parameter ratio	9.01
Goodness-of-fit (GOF) on F^2	0.951
R indices [$I > 2\sigma(I)$]	R_1 = 0.0436, wR_2 = 0.1189
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.93, −1.29

2.6. Catalytic N-arylation of imidazole by binuclear Pd(II) complexes

In a typical N-arylation reaction, $[(PPh_3)_2ClPd(L1)PdCl]$ (0.01 g, 0.01 mmol) was added to a mixture of 4-chlorobenzonitrile (0.137 g, 1 mmol), imidazole (0.088 g, 1.2 mmol) and K_2CO_3 (0.276 g, 2 m mol) in *N*,*N*-dimethyl acetamide (DMAc) (4 cm^3) and stirred at 120 °C. After completion of the reaction (as monitored by TLC), the reaction mixture was extracted with ethyl acetate and quenched with aqueous sodium hydrogen carbonate. The organic layer was separated, dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, 70/30) to afford pure 4-(1H-imidazol-1-yl)benzonitrile. Melting point: 142–144 °C; MS (GC): *m*/*z* 169.06 (M$^+$).

3. Results and discussion

Binuclear Pd(II) complexes were obtained from the reactions of $[PdCl_2(PPh_3)_2]$ with 2-oxoquinoline-3-carbaldehyde Schiff base ligands (H_2L1–H_2L6) in presence of a base, triethylamine (Scheme 1). The complexes are pure and air stable. They are quite soluble in $CHCl_3$, CH_2Cl_2, DMSO and DMF, and insoluble in MeOH and EtOH. The elemental analyses data and melting points of the compounds have been tabulated (Table 2). The results of elemental analyses for the ligands and complexes are in good agreement with the proposed molecular formula. As expected, the ligands are coordinated in a tridentate fashion (ONO/ONS) to palladium ion. In addition to that, the presence of triethylamine promoted deprotonation of the NH of quinoline moiety followed by coordination to another palladium ion resulting in the formation of binuclear Pd(II) complexes.