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Synthesis, characterization and catalytic activity of new bis(*N*-2,6-diphenylphenol-R-salicylaldiminato)Pd(II) complexes in Suzuki-Miyaura and CO_2 fixation reactions

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A series of bulky *N*-2,6-diphenylphenol-R-salicylaldimines (**HL^X**) and their corresponding bis(*N*-2,6-diphenylphenol-R-salicylaldiminato)Pd(II) complexes (**X**), where R = H (**1**), 3-OCH_3 (**2**), 4-OCH_3 (**3**), 5-OCH_3 (**4**), 3-Me (**5**), 5-Me (**6**), 5-$C(CH_3)_3$ (**7**), 3-$C(CH_3)_3$ (**8**) and 3,5-di-$C(CH_3)_3$ (**9**) have been synthesized. Their structures characterized by elemental analyses, IR, UV/vis, ^1H NMR and ^{13}C NMR spectroscopic techniques. X-ray crystallography shows that complex **3** crystallizes in the triclinic P-1space group with one *trans*-$[PdL^3{}_2]$ molecule and two acetic acid ($C_2H_4O_2$) molecules in the unit cell. All X compounds are proved to be as efficient homogeneous catalysts for both Suzuki-Miyaura cross-coupling reactions of various aryl bromides and cyclic carbonates synthesis from CO_2 and epoxides are reported under appropriate conditions (2 h, 100 °C and 1.6 MPa pressure) without use of phosphine ligands.

1. Introduction

The coordination chemistry of transition metal complexes with salicyladimine ligands on the basis of bulky *tert*-butylphenol moieties has achieved a considerable attention in the last decades, because of their unusual structural, magnetic properties, redox-chemistry and their usage as models for metalloproteins [1–6], as catalysts for the polymerization, copolymerization, epoxidation and hydrogenation of simple olefins and C–C *cross*-coupling reactions [7–11]. The steric and electronic effects of substituent on the salicylaldimine ligands are the key factors in catalytic and redox reactivity [1,6]. Among metal-catalyzed C–C coupling reactions the Pd-catalyzed Suzuki–Miyaura (SM) coupling reaction is one of the most widely used methods for the designing of C–C coupling bonds formation reactions. The SM cross-coupling reaction of aryl halides with organoboron reagents is becoming one of the most important methods for the construction of biaryls, which are present in a wide range of natural products [10], pharmaceuticals, agrochemicals and functional polymer materials [7–11]. Bulky phosphine ligands are mostly used as catalysts in the palladium catalyzed SM cross-coupling reaction [10–14]. However, many phosphines are air and moisture sensitive, toxic and therefore difficult to handle. Recently, alternative ligands such as *N*-heterocyclic carbenes [15], as well as ligand-free systems [16], have been employed in Suzuki coupling reactions. Various nitrogen bearing ligands, such as amines [17], diazabutadienes [18] and salicylaldimines [19], have attracted considerable interest due to their stability and excellent activity. In addition, nitrogen-based ligands are generally non-toxic, robust in nature, insensitive to air/moisture, easy-to-handle, and have the potentiality to overcome some of the drawbacks faced by traditional phosphine ligands [20]. Moreover, electronic and steric properties of salicylaldimine ligands could be easily tuned by properly selecting the condensing partners. Indeed, there have been few reports about employment of sterically hindered phenol bearing ligands in palladium-catalyzed SM reactions [21].

Carbon dioxide is an attractive C_1 feedstock as it is renewable, inexpensive from the viewpoint of green chemistry and atom economy, and can replace commonly used toxic C_1 building blocks, such as phosgene [22,23]. One of the way of the conversion of carbon dioxide and epoxides to afford five-membered cyclic carbonates under appropriate conditions represents encouraging technologies for CO_2 utilization (Scheme 1).

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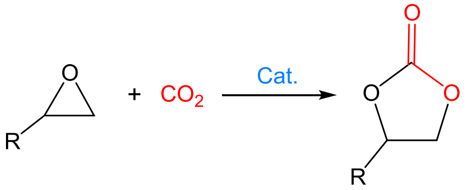

Scheme 1. Atom economic synthesis of cyclic carbonates from various epoxides and CO_2.

As part of our interest in designing new, easily prepared sterically hindered redox active ligands and studying their coordination behavior and catalytic applications, we report herein the synthesis and characterization of a series of palladium complexes with bidentate salicylaldimine ligands derived from X-salicylaldehydes (X = H, CH_3, CH_3O and $C(CH_3)_3$) and 4-amino-2,6-di-phenylphenol and examined their structure and catalytic activity both SM cross-coupling and chemical fixation reactions of CO_2 to yield cyclic carbonates.

2. Experimental

2.1. Materials

R-salicylaldehyde derivatives, R = H, 3-OCH_3, 4-OCH_3 5-OCH_3, 3-CH_3, 5-CH_3, 3-$C(CH_3)_3$, 5-$C(CH_3)_3$, 3,5-di-$C(CH_3)_3$, 2,6-diphenyl-4-aminopenol, 2,4-di-*tert*-butylphenol, $Pd(OAc)_2$, 4-bromoacetophenone, bromobenzene, 4-bromoanisole, 1-bromo-4-nitrobenzene, phenylboronic acid, epichlorohydrin (ECH),1,2-epoxybutane(EB), propylene oxide (PO), styrene oxide (SO), dimethylaminopyridine (DMAP) and cyclohexeneoxide and all solvents, were purchased from Sigma-Aldrich, and Merck. All reagents were used without further purification. The 3,5-di-*tert*-butylsalicylaldehyde was prepared according to the Jacobsen method [24].

2.2. Measurements

The C, H, N elemental analyses were performed on a LECO CHNS-932 model analyzer at the Scientific and Technological Research Center, Inonu University of Turkey. UV-Visible spectra were measured on a Perkin-Elmer Lambda 25 spectrometer operating between 200 and 1100 nm. The IR spectra (without KBr pellet) were recorded on a Perkin-Elmer FT-IR spectrometer in the 450–4000 cm^{-1} region. The ^{1}H {^{13}C} NMR spectra were recorded in $CDCl_3$with a VNMRS-400 “Agilent-NMR” spectrometer at 400 and 100 MHz respectively, without internal standard. Single-crystal structure data were collected with a four-circle Rigaku R-AXIS RAPID-S diffractometer using Mo Kα (0.71073 Å) radiation at 293(2) K. Catalytic CO_2 transformation reactions were performed in a PARR 4591 25 ml stainless pressure reactor. The mixture was separated by centrifugation, and the liquid phase was subjected to GC (Agilent 7820A) analysis with ethylene glycol di-butyl ether as internal standard and hydrogen as the carrier gas.

2.3. Synthesis of 1–9 complexes

The ligands were synthesized by refluxing of the 2,6-diphenyl-4-aminopenol with corresponding salicylaldehyde derivatives in a 1:1 M ratio in ethanol solutions as recently described [25]. The $Pd(\mathbf{L^X})_2$ complexes were prepared as fellows. Pd(II) acetate (0.122 g, 0.5 mmol) was added as a solid to stirring warm solution of $\mathbf{HL^X}$ (1 mmol) in acetic acid (10 ml) and $CHCl_3$ (25–30 ml). The resulting mixture was heated at ca. 45–50 °C on water bath for about 2 h. In most cases after 3–5 min stirring, the appearance of orange or red precipitates was observed. The volume of the reaction mixture was reduced to 2–3 ml and precipitated solids were collected by vacuum filtration, washed with cold water/methanol solution and dried in air. The obtained compounds were recystallized from methanol/$CHCl_3$ mixture (2:3). Slow evaporation of a solution of **3** in $CH_3CN/CHCl_3$ mixture (1:1) at room temperature afforded orange crystals suitable for X-ray diffraction analysis. Unlike of our all efforts, we were not able to grow crystals suitable for X-ray analysis for **1**, **2**, **4**–**9** complexes. Some physicochemical characteristics of **1**–**9** are given in Table 1.

2.3.1. *Bis[N-(2,6-diphenylphenol)salicylaldiminato]Pd(II) (**1**)*

Yield: 65%. ^{1}H NMR (VNMRS-400 MHz, $CDCl_3$)δ: 8.5 (s, 2H, C*H*=N), 8.2 (s, 2H, C*H*=N), 7.60 (d, *J* = 8.0 Hz, 6H), 7.42(t, *J* = 8 Hz 8 H, Ph), 7.32 (d, *J* = 7.2 Hz, 7.05 (td, J_1 = 8.8 Hz, J_2 = 1.6 Hz, 2H, Ph), 6.47 (t, *J* = 7.2 Hz, 2H, Ph), 6.07 (d, *J* = 8.8 Hz, 2H, Ph), 5.46 (s, 2H, O*H*). ^{13}C NMR (VNMRS-400 MHz, $CDCl_3$) δ: 162.62 (*C*H=N), 149.62 ($C_{1aniline}$-OH), 146.48 (C_{2sal}-O), 143.59($C_{4aniline}$-N), 138.10 (C_{1sal}), 135.74($C_{3\ sal}$), 132.48 (Ph-C_4 sal), 129.89 (Ph-C_5 sal), 128.93 (Ph-*C*), 128.0 (Ph-*C*), 127.64 (Ph-*C*), 124.92 (Ph-*C*), 120.57 (Ph-*C*), 119.66 (Ph-*C*).

2.3.2. *Bis[N-(2,6-diphenylphenol)-3-CH_3O-salicylaldiminato] Pd(II)(**2**)*

Yield: 78%.^{1}H NMR (VNMRS-400 MHz, $CDCl_3$) δ: 7.70 (s, 2H, C*H*=N), 7.63 (d, *J* = 6.8 Hz, 6H), 7. 47(t, J = 7.2 Hz 6 H, Ph), 7.39 (d, *J* = 6.0 Hz, 2H, Ph), 7.25 (d, *J* = 6.0 Hz, 4H, Ph), 7.05 (d, *J* = 8.8 Hz, 2H, Ph), 5.76 (s, 2H, O*H*), 3.5 (s, 6H, C*H*$_3$O). $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ: 166.19 (*C*H=N), 165.39(*C*H=N), 162.50 ($C_{1aniline}$-OH), 148.98 (C_2sal-O), 142.98 ($C_{4aniline}$-N), 138.87 (C_3sal-OCH_3), 136.86 (C_4sal), 130.69 (C_3anilime), 129.83 (Ph-*C*), 127.47 (Ph-*C*), 126.47 (Ph-*C*), 114.92 (Ph-*C*), 106.05 (Ph-*C*), 101.08 (Ph-*C*), 55.31 (OCH_3), 21.49 (OCH_3).

Table 1
Physical properties of the **1**–**9** complexes.

Com- pound	Color	M.p. °C	Empirical formula	Found(Calcd.) (%)		
				C	H	N
1	green	>280	$C_{50}H_{36}N_2O_4Pd$	72.19 (72.15)	4.75(4.85)	3.26(3.36)
2	orange	>282[a]	$C_{52}H_{40}N_2O_6Pd$	69.26(69.76)	4.52(4.51)	3.26(3.13)
3	orange	>280	$C_{56}H_{48}N_2O_{10}Pd$	66.36(66.24)	4.68(4.76)	2.56(2.76)
4	orange	>278[a]	$C_{52}H_{40}N_2O_6Pd$	69.36(69.76)	4.32(4.51)	3.21(3.13)
5	orange	>280	$C_{52}H_{40}N_2O_4Pd$	72.46(72.34)	4.82(4.68)	3.36(3.24)
6	orange	>280	$C_{52}H_{40}N_2O_4Pd$	72.26(72.34)	4.52(4.68)	3.34(3.24)
7	red	>253[a]	$C_{58}H_{52}N_2O_4Pd$	73.43(73.52)	5.42(5.54)	3.06(2.96)
8	red	>280	$C_{58}H_{52}N_2O_4Pd$	71.16(71.11)	5.62(5.31)	3.06(2.86)
9	green	>292	$C_{66}H_{68}N_2O_4Pd$	74.66(74.81)	6.32(6.48)	2.58(2.64)

[a] Decomposition.