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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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ABSTRACT

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, ^{1}H 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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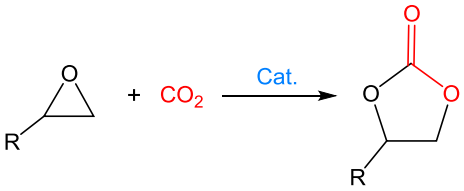


Scheme 1. Atom economic synthesis of cyclic carbonates from various epoxides and CO_2.

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 $^1H\{^{13}C\}$ 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%. ^1H NMR (VNMRS-400 MHz, $CDCl_3$)δ: 8.5 (s, 2H, *CH*=N), 8.2 (s, 2H, *CH*=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 (*CH*=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%.^1H NMR (VNMRS-400 MHz, $CDCl_3$) δ: 7.70 (s, 2H, *CH*=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, CH_3O). $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ: 166.19 (*CH*=N), 165.39(*CH*=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.

*2.3.3. Bis[N-(2,6-diphenylphenol)-4-CH_3O-salicylaldiminato]Pd(II) (**3**)*

Yield: 75%. ^{1}H NMR (VNMRS-400 MHz, $CDCl_3$) δ: 13.4 (s, 2H, COO*H*), 7.80 (s, 2H, C*H*=N), 7.61 (d, *J* = 7.2 Hz, 6H), 7.47 (t, *J* = 7.2 Hz, 4H), 7.39(d, *J* = 6.8 Hz 4 H, Ph-*H*), 7.27 (d, *J* = 20.8 Hz, 6H, Ph-*H*), 6.8 (d, *J* = 6 Hz, 2H, Ph-*H*), 6.26 (d, *J* = 9.2 Hz, 2H, Ph-*H*), 5.5 (s, 2H, O*H*), 3.6 (s, 6H, CH_3O). ^{1}C NMR (VNMRS-100 MHz, $CDCl_3$) δ:172.63 (*C*OOH), 168.25 (*C*=N), 164.53 (*C*H=N), 153.38 (*C*-OH), 153 (C_{4sal}-OCH_3), 147.0 ($C_{4aniline}$-N), 143.6 (C_3sal), 135.5 (C_3sal), 134.60 (C_5sal-*C*), 133.44 (C_5sal-*C*), 132.24 (Ph-*C*), 130.99 (Ph-*C*), 125.7 (Ph-*C*) (Ph-*C*), 124.2 (*C*H_3–C=O), 119.88(*C*H_3–C=O), 60.64(O*C*H_3).

*2.3.4. Bis[N-(2,6-diphenylphenol)-5-CH_3O-salicylaldiminato]Pd(II) (**4**)*

Yield: 75%. ^{1}H NMR (VNMRS-400 MHz, $CDCl_3$)δ: 7.80 (s, 2H, C*H*=N), 7.59(t, *J* = 5.4 Hz, 6-4H), 7.6 (t, *J* = 7.6 Hz, 6H), 7.42 (s, 2H), 7.39 (t, *J* = 4 Hz, 4H), 7.02 (d, *J* = 7.6 Hz, 2H, Ph), 6.4 (t, *J* = 7.4 Hz, 2H, Ph), 5.46 (s, 2H, O*H*), 2.49 (s, 6H, CH_3O). ^{13}C NMR (VNMRS-400 MHz, $CDCl_3$) δ:163.84 (*C*H=N), 163.38($C_{4aniline}$-OH), 156.89 (C_2sal-O), 147.89 ($C_{4aniline}$-N), 143.51(C_3sal), 137.01($C_{3aniline}$), 135.14(C_6sal), 132.35 (Ph-*C*), 129.72 (Ph-*C*), 129.30 (Ph-*C*), 128.99 (Ph-*C*), 128.90 (Ph-*C*), 127.94 (Ph-*C*), 125.0 (Ph-*C*), 119.18 (Ph-*C*), 114.83 (Ph-*C*), 15.60 (*C*H_3O).

*2.3.5. Bis[N-(2,6-diphenylphenol)-3-CH_3-salicylaldiminato]Pd(II) (**5**)*

Yield: 68%.^{1}H NMR (VNMRS-400 MHz, $CDCl_3$) δ: 7.80 (s, 2H, C*H*=N), 7.62 (d, *J* = 7.2 Hz, 8H Ph), 7.48 (t, *J* = 7.2 Hz, 8H), 7.39 (t, *J* = 7.2 Hz, 4H, Ph), 7.26 (d, *J* = 5.6 Hz, 6H), 6.93 (d, *J* = 8.4 Hz, 4H), 6.26 (d, *J* = 5.6 Hz, 2H), 5.5 (s, 2H, O*H*), 2.2 (s, 6H, CH_3). ^{13}C NMR (VNMRS-400 MHz, $CDCl_3$) δ:163.42 (*C*H=N), 162.62 (*C*H=N), 149.62 ($C_{1aniline}$-OH), 147.58(C_{2sal}-O), 142.59($C_{4aniline}$-N), 137.10 (C_{1sal}-CH_{imine}), 136.84($C_{3\ sal}$), 133.38 (Ph-C_4 sal), 129.39 (Ph-C_5 sal), 128.93 (Ph-*C*), 128.17 (Ph-*C*), 127.84 (Ph-*C*), 125.92 (Ph-*C*), 123.83 (Ph-*C*), 120.57 (Ph-*C*), 119.66 (Ph-*C*), 19.99 (*C*H_3).

*2.3.6. Bis[N-(2,6-diphenylphenol)-5-CH_3-salicylaldiminato]Pd(II) (**6**)*

Yield: 55%.^{1}H NMR (VNMRS-400 MHz, $CDCl_3$)δ: 8.7 (s, 2H, C*H*=N), 7.8 (s, 2H, C*H*=N), 7.61–7.60 (dd, *J* = 7.2 Hz, 2H), 7.5 (t, *J* = 8.2 Hz, 6H), 7.44(d, *J* = 1.2 Hz, 4), 7.38 (d, *J* = 1.2 Hz, 2H), 7.22 (d, *J* = 1.2 Hz, 2H), 7.14 (d, *J* = 1.6 Hz, 2 H, Ph), 7.03 (d, *J* = 6.8 Hz, 2H, Ph), 6.87 (t, *J* = 7.6 Hz, 2H, Ph), 6.46 (t, *J* = 7.6 Hz, 2H, Ph), 5.46 (s, 2H, OH), 5.40 (s, 2H, O*H*), 1.46 (s, 3H, CH_3), 0.95 (s, 3H, CH_3). ^{13}C NMR (VNMRS-100 MHz, $CDCl_3$)δ:164.3 (*C*H=N), 152(C_{Ph}-OH), 149 (C_{Ph}-O), 146.4 (C_{Ph}-N), 144.5 (C_{Ph}-N), 141.6 (C_{sal}-CH_{imine}), 137.4 (C_{sal}-CH_{imine}), 132.7 (C_{sal}), 129.39 (C_{sal}), 129.29 (C_{sal}), 129.02(C_{sal}), 128.99 (C_{sal}), 128.03 (C_{sal}-*C*), 122.59(Ph-*C*), 117.23 (Ph-*C*), 114.45(Ph-*C*), 110.78(Ph-*C*), 66.89(Ph-*C*), 64.08(Ph-*C*), 29.32(*C*H_3), 28.93(*C*H_3).

*2.3.7. Bis[N-(2,6-diphenylphenol)-5-tert-butylsalicylaldiminato] Pd(II) (**7**)*

Yield: 65%.^{1}H NMR (VNMRS-400 MHz, $CDCl_3$) δ: 7.85 (s, 2H, C*H*=N), 7.61–7.26 (m), 6.81 (d, *J* = 7.6 Hz, 2H, Ph), 6.63 (d, *J* = 6.8 Hz, 2H, Ph), 6.57 (d, *J* = 6.8 Hz, 2H, Ph), 6.47 (d, *J* = 6.0 Hz, 2H, Ph), 6.2 (t, 2H, *J* = 6.8 Hz, 2H, Ph), 6.1 (d, *J* = 7.2 Hz, 2H, Ph), 5.52 (s, 2H, O*H*), 5.45 (s, 2H, O*H*), 2.1 (s, 9 H, C(CH_3)$_3$, 1.38 (s, 9 H, C(CH_3)$_3$. ^{13}C NMR (VNMRS-100 MHz, $CDCl_3$) δ:163.5 (*C*H=N), 162.9 (*C*H=N), 156.6 ($C_{1aniline}$-OH), 151.3 (C_{2sal}-O), 147.6 ($C_{4aniline}$-N), 142.95(C_{3sal}), 142.68 (C_4sal), 137.41(C_6sal), 137.34 (Ph-*C*), 137.17 (Ph-*C*), 127.74 (Ph-*C*), 125.76 (Ph-*C*), 120.51(Ph-*C*), 119.90 (Ph-*C*), 114.60 (Ph-*C*), 114.19 (Ph-*C*), 55.51 (Ph-*C*), 33.58 (5-OCH_3), 29.71(5-OCH_3).

*2.3.8. Bis[N-(2,6-diphenylphenol)-3-tert-butylsalicylaldiminato] Pd(II)(**8**)*

Yield: 65%.^{1}H NMR (VNMRS-400 MHz, $CDCl_3$)δ: 7.82 (s, 2H, C*H*=N), 7.6 (d, *J* = 6.8 Hz, 6H, Ph), 7.51 (t, *J* = 7.2 Hz, 6H, Ph), 7.43 (t, *J* = 7.2 Hz, 2H, Ph), 7.15 (d,d, J_1 = 6.8 Hz, J_2 = 1.2 Hz, 2H, Ph), 7.0 (d,d, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 2H, Ph), 6.47 (t, *J* = 7.2 Hz, 2H, Ph), 5.4 (s, 2H, O*H*), 0.95 (s, 18 H, C(CH_3)$_3$). ^{13}C NMR (VNMRS-100 MHz, $CDCl_3$) δ:165.11(*C*H=N), 163.64 ($C_{1aniline}$-OH), 148.54 (C_{2sal}-O), 144.22 ($C_{4aniline}$-N), 140.37 (C_3sal), 132.92(C_3aniline), 131.86(Ph-*C*), 129.38(Ph-*C*), 129.01 (Ph-*C*), 128.99 (Ph-*C*), 127.97 (Ph-*C*), 125.93 (Ph-*C*), 122.17(Ph-*C*), 114.83 (Ph-*C*), 34.68 (*C*(CH_3)$_3$), 28.69 (C(*C*H_3)$_3$).

*2.3.9. Bis[N-(2,6-diphenylphenol)-3,5-di-tert-butylsalicylaldiminato]Pd(II)(**9**)*

Yield:65 4%. ^{1}H NMR (VNMRS-400 MHz, $CDCl_3$)δ: 7.80 (s, 2H, C*H*=N), 7.3 (t, *J* = 6.8 Hz, 6H, Ph), 7.51 (t, *J* = 7.2 Hz, 4H, Ph), 7.43 (t, *J* = 7.2 Hz, 2H, Ph), 7.23 (d, J_1 = 6.8 Hz, J_2 = 1.2 Hz, 2H, Ph), 7.0 (d, *J* = 2.0 Hz, 2H, Ph), 6.9 (d, *J* = 2 Hz, 2H, Ph), 5.4 (s, 2H, O*H*), 1.55 (s, 18 H, C(CH_3)$_3$), 0.96 (s, 18 H, C(CH_3)$_3$). ^{13}C NMR (VNMRS-100 MHz, $CDCl_3$) δ:163.5 (*C*H=N), 162.9 (*C*H=N), 156.6 ($C_{1aniline}$-OH), 151.3 (C_{2sal}-O), 147.6(C_{2sal}-O), 142.95 ($C_{4aniline}$-N), 142.68 ($C_{4aniline}$-N), 137.41(C_3sal), 137.34 (C_5sal), 137.17 (C_6sal), 127.74 (Ph-*C*), 125.76 (Ph-*C*), 120.51(Ph-*C*), 119.90 (Ph-*C*), (Ph-*C*), 114.60 (Ph-*C*), 114.19 (Ph-*C*), 33.58 (5-OCH_3), 29.71(5-OCH_3).

2.4. X-ray crystallographic data

For the crystal structure determination, the single-crystals of the complexes *trans*-[PdL^3_2]·2$C_2H_4O_2$ were used for data collection on a four-circle Rigaku R-AXIS RAPID-S diffractometer (equipped with a two-dimensional area IP detector). The graphite-monochromatized Mo K_α radiation (λ = 0.71073 Å) and oscillation scans technique with Δω = 5° for one image were used for data collection. The lattice parameters were determined by the least-squares methods on the basis of all reflections with $F^2 > 2\sigma(F^2)$. Integration of the intensities, correction for Lorentz and polarization effects and cell refinement was performed using Crystal Clear (Rigaku/MSC Inc., 2005) software [26]. The structures were solved by direct methods using SHELXS-97 [27] and refined by a full-matrix least-squares procedure using the program SHELXL-97 [27]. H atoms were positioned geometrically and refined using a riding model. The final difference Fourier maps showed no peaks of chemical significance.

2.5. Catalytic activity measurements

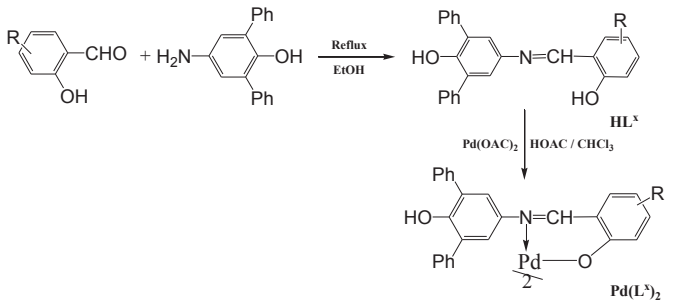
Two different types of catalytic studies (SM and CO_2-epoxide coupling reactions) were performed.

2.5.1. SM coupling reactions

All reactions were performed using Schlenk-type flask under nitrogen gas. Pd(II) complex (1.5% mmol), phenylboronic acid (1.5 mmol), aryl halides (1 mmol), base (1.5 mmol) and solvent (3 ml) were added in to a Schlenk tube under nitrogen atmosphere. The Schlenk tube was stirred at 80 °C for desired hours. The reaction mixture was then cooled to room temperature, diluted with CH_2Cl_2 and filtered through on celite. The yield of reaction was determined by GC (Agilent 7820A).

2.5.2. CO_2-epoxide coupling reactions

A 25 ml stainless pressure reactor was charged with complex (4.5×10^{-5} mol), epoxide (4.5×10^{-2} mol), and DMAP (9×10^{-5} mol). The reaction vessel was placed under a constant pressure of carbon dioxide for 2 min to allow the system to



R = H (**HL**[1]), 3-OCH_3 (**HL**[2]), 4-OCH_3 (**HL**[3]), 5-OCH_3 (**HL**[4]), 3-CH_3 (**HL**[5]), 5-CH_3 (**HL**[6]), 5-$C(CH_3)_3$ (**HL**[7]), 3-$C(CH_3)_3$ (**HL**[8]) and 3,5-di-$C(CH_3)_3$ (**HL**[9]). Corresponding complexes $Pd(L^x)_2$ abbreviated as **1-9.**

Scheme 2. Synthetic procedure of complexes **1**–**9**.

equilibrate and CO_2 was charged into the autoclave with desired pressure then heated to the desired temperature. The pressure was kept constant during the reaction. The vessel was then cooled to 5–10 °C in ice bath after the expiration of the desired time of reaction. The pressure was released, then, the excess gases were vented. The yields of epoxides to corresponding cyclic carbonates were determined by GC (Agilent 7820A).

3. Results and discussion

The synthesizes of salicylaldimine ligands, **HL**[1]-**HL**[9], and their analytical, IR, UV/Vis, ^1H and ^{13}C NMR spectroscopic characteristics were described in a previous report [25]. While the synthesis, characterization and redox reactivity behaviors of Pd(II) complexes with **HL**[1] and **HL**[9] ligands were previously reported [28], their ^1H, ^{13}C NMR spectral characterization and catalytic activity properties have not reported, therefore for comparative purposes, their some spectral and physicochemical data are also included in present work. The synthetic procedure of complexes was shown as below (Scheme 2).

3.1. IR spectra

Some characteristic FT-IR data of **1**–**9** are presented in Table 2. The stretching vibrations of the ν(CH═N) group in the IR spectra of

Table 2
IR and electronic spectral data of 1–9 complexes in $CHCl_3$.

Com-pound	Characteristic IR spectral data			Electronic spectra (λ/nm) (logε)
	νC = N, νC = O	νC = C-O	νOH	
1	1605	1536	3514, 3356	290(4.93), 350[a], 380[a], 417(4.54)
2	1604	1543	3538	250(4.7), 303(4.26), 424(4.43)
3	1602, 1750	1534	3537, 3498	254(3.92), 303(4.83), 402(4.44)
4	1601	1538	3449	244(4.64), 320(4.56), 451(4.11)
5	1603	1543	3538	248(4.83), 300[a], 412(3.74)
6	1613	1531	3523	253(4.77), 310(4.33), 430(3.91)
7	1614	1526	3538	244(5.11), 262(4.80), 313(4.78), 353[a], 425(4.2)
8	1608	1542	3533	246(4.8), 260[a], 307(4.49), 406(4.1)
9	1606	1528	3538, 3407	233(4.8), 260(3.9), 307(4.4), 406(4.1)

[a] Shoulder.

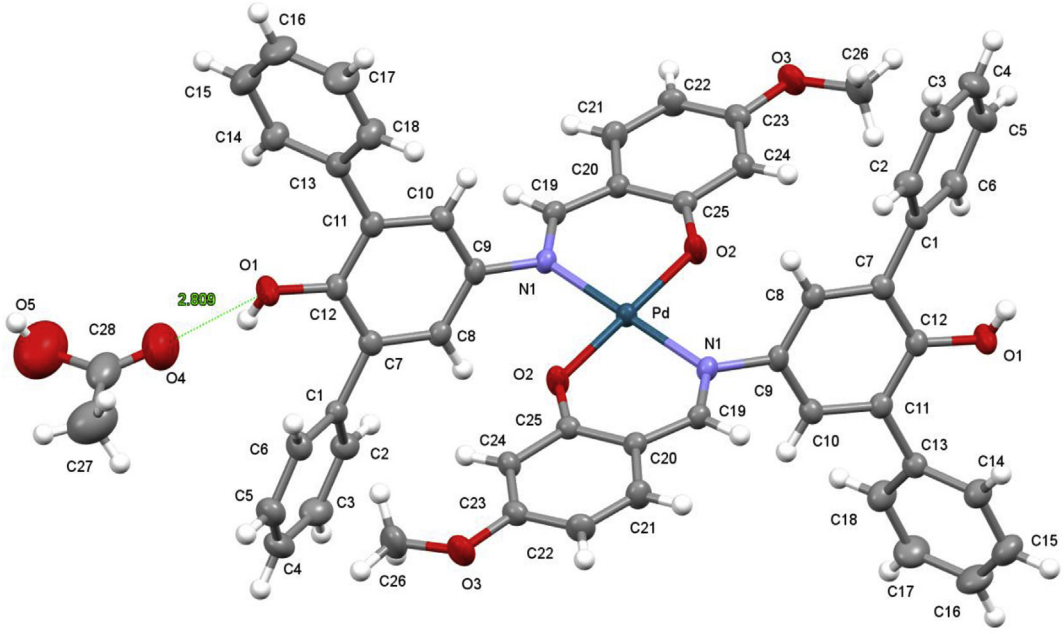
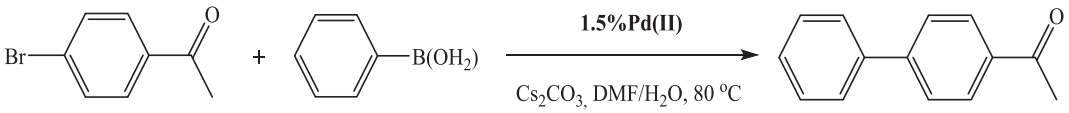


Fig. 1. Molecular structure of *trans*-[PdL^3_2]($C_2H_4O_2$); thermal ellipsoids were drawn at the 40% probability level. Selected bond lengths (Å) and bond angles (°): Pd–O2 1.981(7), Pd–N1 2.029(12), N1-Pd–O291.25(1), N1–C191.291(9), Pd–N1-C19 123.10(4), O1–C12 1.368(4), C25–O2–Pd1 27.75(5), C23-O31.356(4), N1-C9 1.443(4), O4-C281.218(4), C28-O5 1.491.

Table 3
Crystal data and structure refinement.

Empirical formula	$C_{52}H_{40}N_2O_6Pd \cdot 2(C_2H_4O_2)$	
Formula weight	1015.36	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	*P-1*	
Unit cell dimensions	$a = 10.2045(4)$ Å	$\alpha = 76.593(3)^\circ$
	$b = 11.1654(4)$ Å	$\beta = 86.689(2)^\circ$
	$c = 12.2134(5)$ Å	$\gamma = 64.112(2)^\circ$
Volume	1216.30(9) $Å^3$	
Z	1	
Density (calculated)	1.386 Mg/m^3	
Absorption coefficient	0.444 mm^{-1}	
F(000)	524	
θ range for data collection	1.7–28.5°	
Index ranges	$-13 \le h \le 13$, $-14 \le k \le 14$, $-14 \le l \le 16$	
Reflections collected	29706	
Independent reflections	5751 [$R_{int} = 0.043$]	
Completeness to $\theta = 28.50^\circ$	98.7%	
Refinement method	Full-matrixleast-squares on F^2	
Data/restraints/parameters	5104/3/315	
Goodness-of-fit on F^2	1.210	
Final *R*indices [$F^2 > 2\sigma(F^2)$]	$R1 = 0.063$, $wR2 = 0.134$	
*R*indices (all data)	$R1 = 0.082$, $wR2 = 0.146$	
Largest difference in peak and hole	1.799 and −1.052 e $Å^{-3}$	

Table 4
Suzuki coupling reaction of 4-bromoacetophenone with phenylboronic acid.

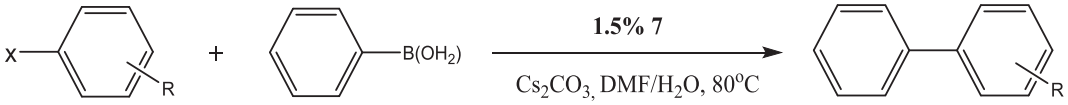


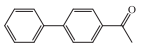
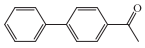
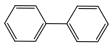
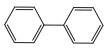
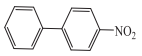
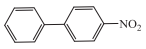
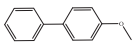
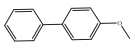
Entry	Catalysts	Solvent	Time (h)	Yield[a](%)
1	**1**	DMF/H_2O(4:1)	2	96
2	**1**	DMF/H_2O(4:1)	4	91
3	**2**	DMF/H_2O(4:1)	2	96
4	**2**	DMF/H_2O(4:1)	4	91
5	**3**	DMF/H_2O(4:1)	2	98.7
6	**3**	DMF/H_2O(4:1)	4	98.3
7	**4**	DMF/H_2O(4:1)	2	98.9
8	**4**	DMF/H_2O(4:1)	4	98
9	**5**	DMF/H_2O(4:1)	2	98.1
10	**5**	DMF/H_2O(4:1)	4	98
11	**6**	DMF/H_2O(4:1)	2	98.4
12	**6**	DMF/H_2O(4:1)	4	98
13	**7**	DMF/H_2O(4:1)	2	99.7
14	**7**	DMF/H_2O(4:1)	4	97.4
15	**8**	DMF/H_2O(4:1)	2	98.8
16	**8**	DMF/H_2O(4:1)	4	97.9
17	**9**	dioxane	2	90
18	**9**	dioxane	4	95
19	**9**	DMF/H_2O(4:1)	2	99.2
20	**9**	DMF/H_2O(4:1)	4	99

Reaction conditions: 1.5 mmol % Pd, 1 mmol 4-bromoacetophenone, 1.5 mmol phenylboronic acid, 3 mL solvent (DMF(4)/H_2O(1)-dioxane), heat (80 °C), base (Cs_2CO_3).
[a] The yields checked by GC analysis.

1–**9** were detected in the 1601–1614 cm^{-1} region and shifted to lower frequencies relative to corresponding free **HL^x** (1613–1619 cm^{-1}), indicating that the coordination has taken place through the azomethine nitrogen atom of the ligands to palladium metal ion. A weak broad feature centered at 2500–2800 cm^{-1}, due to ν(OH) of the intramolecularly H-bonded OH•••N in **HL^x**, disappears in the spectra of all the complexes, suggesting their coordination via deprotonated phenolic oxygen atom to Pd(II). The sharp strong band appeared in the 3514–3538 cm^{-1} range has been assigned to stretching frequency of the sterically hindered νOH in the **1**, **2** and **4**–**9** complexes. In the IR spectrum of **3** unlike of other complexes along with intense broad peak at 1750 cm^{-1} assignable to ν(C═O) of CH_3COOH**,** an intense narrow band at 3498 cm^{-1} and a middle intensity very broad band centered at 3449–3537 cm^{-1} were observed (Table 2). These peaks are assigned to νOH of the sterically hindered OH of **3** and intermolecular OH···O between CH_3COOH and **3** molecules, respectively. A sharp strong peak observed at 3449 cm^{-1} in the IR spectrum of **4** is assigned to νOH of the intermolecularly bonded OH groups. A new bands appeared within ranges of 1526–1543, 530–562 and 479–505 cm^{-1} detected

Table 5
Suzuki coupling reactions of aryl halides with phenylboronic acid.



Entry	Catalysts	Arylhalide	Product	Time (h)	Yield[a](%)
1	**7**	4-bromoacetophenone		1	98.8
2	**7**	4-bromoacetophenone		2	97.9
3	**7**	bromobenzene		1	99.3
4	**7**	bromobenzene		2	100
5	**7**	1-bromo-4-nitrobenzene		1	99.4
6	**7**	1-bromo-4-nitrobenzene		2	100
7	**7**	4-bromoanisole		1	94.6
8	**7**	4-bromoanisole		2	99.7

Reaction conditions: 1.5 mmol % **7**, 1 mmol arylhalide, 1.5 mmol phenylboronic acid, 3 mL solvent (DMF(4)/H_2O(1)), heat (80 °C), base (Cs_2CO_3).
[a] The yields checked by GC analysis.

Table 6
Suzuki coupling reactions of 1-bromo-4-nitrobenzene with phenylboronic acid in the presence of inorganic bases.

Entry	Catalysts	Base	Time (h)	Yield[a](%)
1	**7**	Na_2CO_3	1	99.7
2	**7**	Na_2CO_3	2	100
3	**7**	K_2CO_3	1	100
4	**7**	K_2CO_3	2	100
5	**7**	Cs_2CO_3	1	99.4
6	**7**	Cs_2CO_3	2	100

Reaction conditions: 1.5 mmol % **7**, 1 mmol 1-bromo-4-nitrobenzene, 1.5 mmol phenylboronic acid, 3 ml solvent (DMF(4)/H_2O(1)), heat (80 °C).
[a] The yields checked by GC analysis.

in the spectra of all **1**–**9** compounds are assigned to νC = C–O, νPd-N and νPd-O vibrations, respectively [29].

3.2. Electronic absorption spectra

The UV/vis spectral data for all **1**–**9** complexes were obtained using $10^{-3} \pm 10^{-5}$ M solutions in the $CHCl_3$ in the 200–1100 nm range (Table 2). The electronic spectra of **1**–**9** in $CHCl_3$ (Table 2) exhibit very intense similar bands at 245–380 nm region and were assigned to intraligand n → π* and π → π* transitions. The very intense bands appeared within 390–440 nm region according to their higher molar coefficient extinctions (logε = 3.91–4.54 M^{-1} cm^{-1}) were assigned to a spin allowed charge transfer (MLCT) transitions [30,31].

3.3. ^1H and ^{13}C NMR spectra

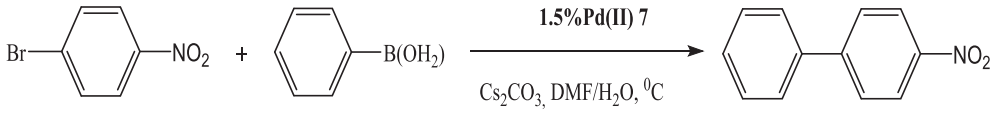
The ^1H and ^{13}C NMR spectroscopic data and their interpretation were described in the Experimental section. The ^1H NMR and ^{13}C NMR spectral parameters of **1**–**9** complexes shows that their aromatic, azomethine and CH_3 groups protons signals were shifted to high field positions comparing to those in the uncomplexed free **HL^1**-**HL^9** ligands.

3.4. Molecular structure description

3.4.1. Single crystal X-ray diffraction studies of complex 3

Single crystals of complex **3** suitable for X-ray crystallographic analysis were grown from a saturated acetonitrile/chloroform solution at room temperature over a period of two days through slow evaporation of the solvent. The complex crystallizes in a triclinic system with a P-1space group, with one *trans*-[**PdL^3_2**] molecule and two acetic acid (*trans*-**PdL^3_2**·$2C_2H_4O_2$) molecules in the unit cell. The asymmetric unit of this compound consists of one half-molecule of *trans*-[**PdL^3_2**] and one acetic acid molecule. The molecular structure is depicted in Fig. 1 and the crystal data are given

Table 7
Suzuki coupling reactions of 1 mmol 1-bromo-4-nitrobenzene with phenylboronic acid under various temperature and times.



Entry	Catalysts	Heat (^{0}C)	Time (h)	Yield[a](%)
1	**7**	80	1	99.4
2	**7**	80	2	100
3	**7**	25	1	4
4	**7**	25	2	7.5
5	**7**	25	4	12
6	**7**	25	6	13
7	**7**	25	24	20

Reaction conditions: 1.5 mmol % **7**, 1 mmol 1-bromo-4-nitrobenzene, 1.5 mmol phenylboronic acid, 3 ml solvent (DMF(4)/H_2O(1)), base (Cs_2CO_3).
[a] The yields checked by GC analysis.

in Table 3. In this complex, each Schiff base ligand (**HL^3**) is bonded to the Pd(II) center through nitrogen atom and oxygen atom, providing two equivalent six-member N-Pd-O-C-chelate rings. The geometry at the Pd(II) center in **3** is square planar, with the two cyclometalated ligands in a *trans* arrangement. The Pd–O and Pd–N distances are 1.980(3) and 2.028(4) Å, similar to those seen in related complexes [20,32,33].

The bite angle [N1–Pd–O2 = 91.26(4)°] is in good agreement with those found in a structurally related mononuclear complex with salicylaldiminato ligands as bridging ligands [32–35]. The imine C=N bonds in complex **3** retain their double bond character, being 1.292(6) Å (C19 = N1)) in length.

The square-planar *trans*-[**PdL$^3_2$**] complex did not display any close metal-metal or π-π interactions in the crystal lattice. Instead, it showed 1D polymeric stacking of turned sheets consisting of C-H···O hydrogen bonds along the *b*-axis and the acetic acid molecule was stacked between *trans*-[**PdL$^3_2$**] complex units via O-H···O hydrogen bonds (See Supplementary Data).

The square-planar *trans*-[**PdL$^3_2$**] complex did not display any close metal-metal or π-π interactions in the crystal lattice. Instead, it showed 1D polymeric stacking of turned sheets consisting of C-H···O hydrogen bonds along the *b*-axis and the acetic acid molecule was stacked between *trans*-[**PdL$^3_2$**] complex units via O-H···O hydrogen bonds (See Supplementary Data).

3.5. Catalytic activity studies

3.5.1. SM coupling reactions

The palladium complexes (**1**–**9**) were tested as catalysts for the Suzuki coupling reactions to give the biaryl derivative compounds. We initially studied the reaction of phenylboronic acid with 4-bromoacetophenone in DMF/H_2O as a model reaction under heating to 80 °C in the presence of 1.5 mmol% of Pd(II) metal catalysts and 1.5 mmol of bases. The results are summarized in Table 4. All catalytic reactions were carried out in inert atmosphere.

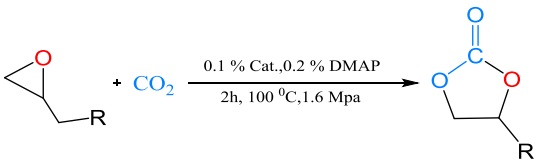
As can be seen from Table 4, among **1**–**9** compounds salicylaldiminato-palladium complexes having 5-*tert*-butyl (**7**) and 3,5-di-*tert*-butyl substituent (**9**) were found to be most active catalysts for the SM cross-coupling reactions. In order to find optimum conditions different substrates (4-bromoacetophenone, bromobenzene, 1-bromo-4-nitrobenzene, 4-bromoanisole) has been performed with phenylboronic acid as model compounds. As shown in Table 5, 1-bromo-4-nitrobenzene was found to be the most reactive aryl halide, while 4-bromoanisole exhibited the lowest activity of the epoxides surveyed. According to Tables 4 and 5, the yield was increased with increasing time.

Effect on the reactions of the bases (Cs_2CO_3, K_2CO_3, Na_2CO_3) has been investigated and it has been found that these bases nearly exhibit the same effect (Table 6). In addition, reaction temperature had positively affected to the reaction yield (Table 7).

3.5.2. CO_2-epoxide coupling

Since the sterically hindered salen-type transition metal complexes exhibits excellent catalysts in the coupling reactions of CO_2 and epoxides, which provide formation of polycarbonates or cyclic carbonates [36], we have interested to study the catalytic efficiency of the **1**–**9** complexes in the coupling of CO_2 with epoxides as shown in Scheme 3. To the best of our knowledge this study is the first study of using bidentate sterically hindered salicylaldimine palladium complexes as catalysts for CO_2 transformations into the cyclic carbonates.

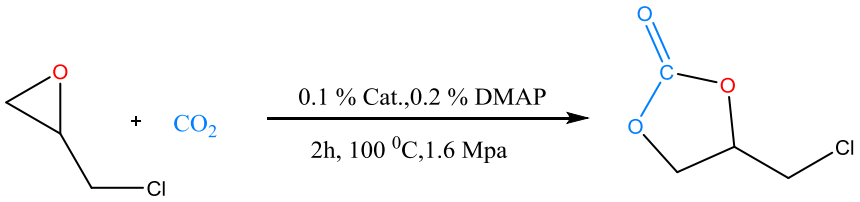
We have carried out catalytic reactions changing the temperature, time, base, pressure and epoxide to find the best reaction conditions. Firstly, the experiments of other epoxides with CO_2 to synthesize the corresponding cyclic carbonates were investigated. The epichlorohydrin (ECH), 1,2-epoxybutane(EB), propylene oxide (PO), styrene oxide (SO), and cyclohexeneoxide (CHO) were tested as substrates. As can be seen from Table 8 among **1**–**9** complexes, compound **2** exhibits higher value for parameters such as yield, selectivity, TON and TOF. Therefore, the effects of temperature, time and pressure on the above parameters have been tested on the samples of **2**. The comparison of catalysts (**1**–**9**) on the cycloaddition of CO_2 with epoxide ECH at the same catalytic conditions revealed that all complexes exhibit higher yield and selectivity with the formation of cyclic carbonate (Fig. 2).



R = Cl (epichlorohidrin) (ECH), CH_3 (1,2-epoxybutane) (EB), H (propylelen oxide) (PO), Ph (styrene oxde) (SO), (cyclohexeneoxide) (CHO).

Scheme 3. Cycloaddition reaction of $CO_2$with various epoxides catalyzed by **1**–**9** catalysts.

Table 8
The comparison of synthesized complexes in catalytic transformation of CO_2 into cyclic carbonate.



Entry	Cat.	Yield [a](%)	Selectivity[a] %	TON[b]	TOF[c](h1)
1	**1**	88.1	99.9	881	440
2	**2**	89.8	98.0	898	449
3	**3**	80.5	98.6	805	403
4	**4**	88.2	98.8	882	441
5	**5**	83.4	99.0	834	417
6	**6**	85.0	99.0	850	425
7	**7**	81.0	98.4	810	405
8	**8**	76.2	99.0	762	381
9	**9**	79.0	99.5	790	395

Reaction conditions: Cat (4.5×10^{-5} mol), epichlorohydrin (4.5×10^{-2} mol), DMAP (4.5×10^{-5} mol),CO_2(1.6 MPa), 100 °C, 2 h.
[a] Yield and selectivity of epichlorhydrin to corresponding cyclic carbonate were determined by GC.
[b] Moles of cyclic carbonate produced perm ole of catalyst.
[c] The rate is expressed in terms of the turnover frequency {TOF [mol of product (mol of catalyst h)$^{-1}$] = turnovers/h}.

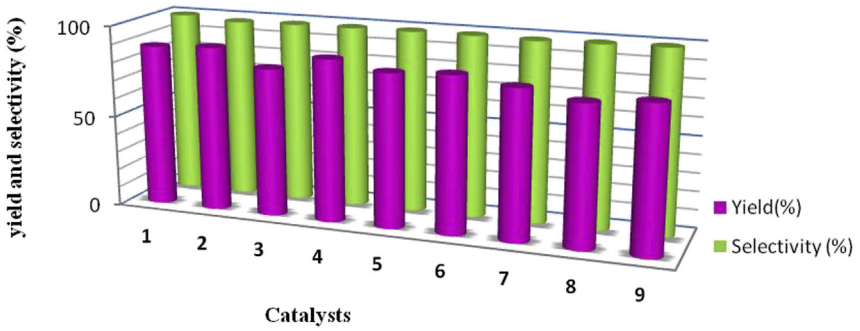


Fig. 2. The comparison of catalysts on the cycloaddition of CO_2 with epichlorohydrin at the same catalytic conditions.

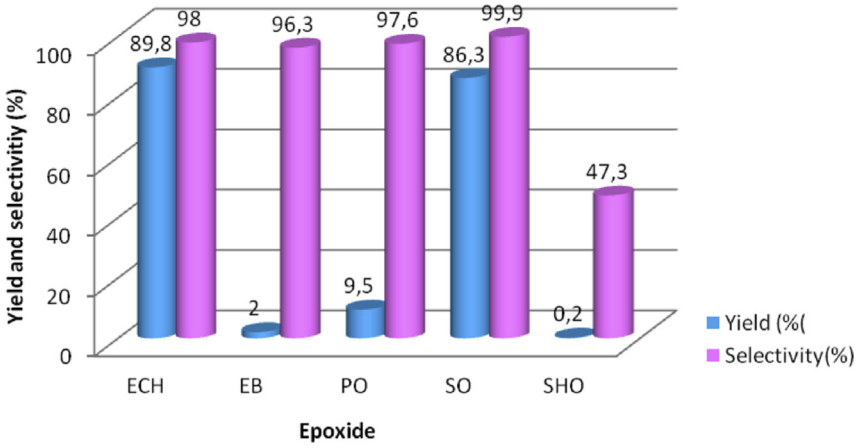


Fig. 3. The comparison of bases on the cycloaddition of CO_2 with ECH at the same catalytic conditions with Pd (II) salicylaldimine complex **(2)** catalyst.

As shown in Fig. 3, the activity order of epoxides was found to be as epichlorohydrin (ECH) > styrene oxide (SO) > cyclohexene oxide (CHO) > 1,2-epoxybutane (EB) > propylene oxide (PO). This result may be due to the more electron donating substituents linked to C_2-atom of these which could be coordinately bonded to the metal center and could be responsible for the catalyst poisoning [37]. Similar effect was observed in our previous studies [35–39].

Fig. 4 shows that the ECHC yield increased with reaction time up to a period 4 h. The cycloaddition reaction proceeds rapidly within

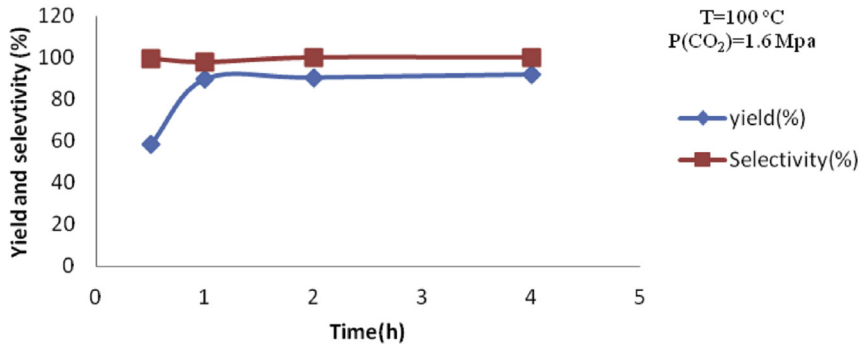


Fig. 4. Conversion and selectivity of ECH as a function of time with **2** as catalyst.

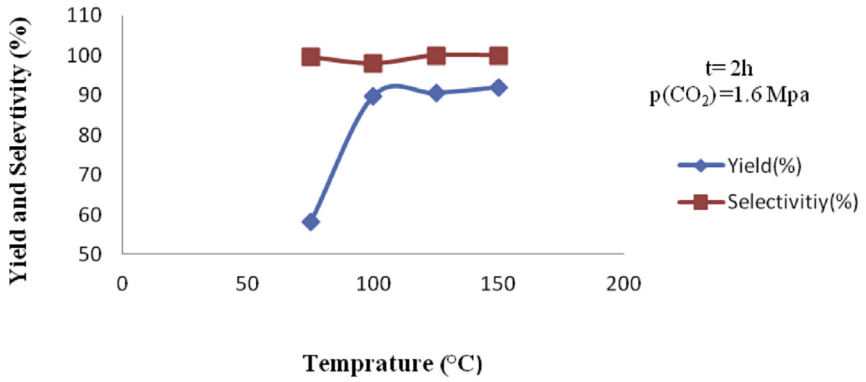


Fig. 5. Conversion and selectivity of ECH as function of temprature using Pd (II) salicylaldimine complex **(2)** as catalyst.

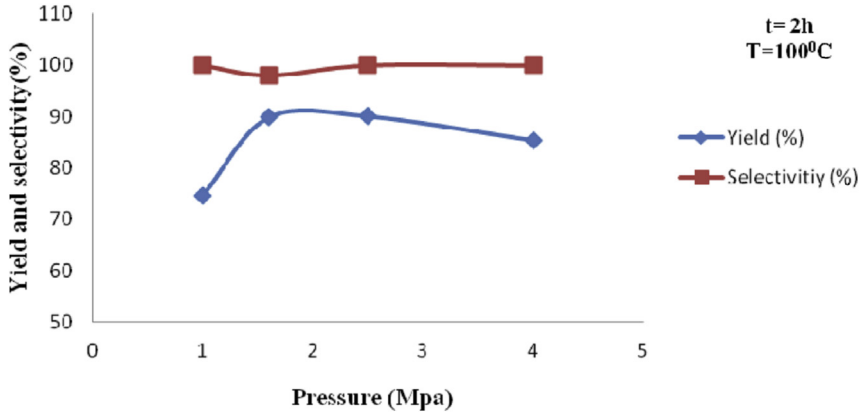


Fig. 6. Conversion and selectivity of ECH as function of pressure using Pd (II) salicylaldimine complex **(2)** as catalyst.

the first 2 h, reaching a ECHC yield of 89.8%. With increase of time from 0.5 to 4 h, ECHC yield increased sharply from 58 to 97.5%. On this basis, the experiments to assess other reaction parameters were performed for 4 h. The results shown in Fig. 5 clearly show that temperature has a strong effect on the ECH conversion. When catalytic reactions were conducted at 75, 100, and 125 °C, the ECH conversions were 99.5, 100.0, and 100.0%, respectively. This temperature and conversion relationship is attributed to higher reactivity at a higher temperature.

As shown in Fig. 6, in the low-pressure range (0.5–2.5 MPa), there is rise of yield (from 71.0% to 90.0%) with increase of initial CO_2 pressure, but further rise of pressure to 4 MPa results in moderate decrease of ECHC yield.

4. Conclusion

In this research, sterically hindered novel palladium(II) salicylaldimine complexes have been successfully synthesized and characterized based on the elemental CHN analysis, spectroscopic techniques and X-ray crystallographic analysis. While all complexes have been prepared in the identical conditions in $CH_3COOH/CHCl_3$, as supported by X-ray, FTIR and ^1H NMR techniques, only complex **3** was crystallized as *trans*-$\mathbf{PdL^3_2}\cdot 2C_2H_4O_2$ solvate molecules. All **1**–**9** compounds are proved to be as an efficient homogeneous catalyst 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. To the best of our

knowledge this study is the first study of using bidentate sterically hindered salicylaldimine palladium complexes as catalysts for atom economic CO_2 fixation into the cyclic carbonates.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2016.03.024.

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