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Structural, spectral, electrochemical and catalytic reactivity studies of a series of N_2O_2 chelated palladium(II) complexes

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ABSTRACT

A series of neutral salicylaldiminato Pd(II) complexes have been synthesized and characterized. Spectral and electrochemical properties of the complexes in the solution phase have been investigated. The structure of complex **9** has been confirmed by X-ray analysis. Spectroscopic characteristics were determined by visible absorption spectra. Cyclic voltammetry analysis has been performed to determine the energy levels of the compounds. The coordination of the Schiff base, according to the spectroscopic techniques, appears to occur through the two azomethine nitrogens and two *o*-OH groups. The salen type Pd(II) complexes have been used as catalysts for the formation of cyclic organic carbonates from carbon dioxide and liquid epoxides, which served as both reactant and solvent. The more electron donating substituents on the backbone and the aryl ring of the ligand system, in particular, effectively promote carbon dioxide activation with liquid epoxides under homogeneous conditions.

1. Introduction

Carbon dioxide (CO_2) is a particularly attractive alternative feedstock as it is inexpensive, highly naturally abundant and the by-product of many industrial applications, including combustion [1]. Carbon dioxide is also attractive as an environmentally friendly chemical reagent and is especially useful as a phosgene substitute [2]. Carbon dioxide fixation has received much attention in recent decades since carbon dioxide is the most inexpensive and infinite carbon resource [3]. Cyclic carbonates are one kind of carbon dioxide fixation product and are widely used as monomers for polymer synthesis, as an aprotic solvent and as a pharmaceutical intermediate [3–6]. The synthesis of cyclic carbonates includes three aspects: catalytic reaction of CO_2 and epoxide, electrochemical reaction of CO_2 and epoxide, and oxidative carboxylation of olefins. Various catalyst systems were developed for the coupling of carbon dioxide and epoxides in the so-called carbon dioxide fixation process, including porphyrins, pathalocyanine, salen metal complexes, metal oxides, zeolite, nanogold, alkali metal salts, ionic liquids and so on [3].

Cyclic carbonates are used industrially as polar aprotic solvents, substrates for small molecule synthesis, antifoam agents for antifreeze, and as plasticizers [7–9]. Tetraalkylammonium salts, phosphanes, main-group and transition-metal complexes, and alkali metals convert epoxides and CO_2 to cyclic carbonates [10]. According to previous studies, only a few metals are active for the coupling of epoxides and CO_2, including Al, Cr, Co, Mg, Li, Zn, Cu and Cd [11–13].

Optimization of the catalytic activities for a given process is typically achieved through the methodical tailoring of the metal's ligand environment. Therefore, ligand frameworks, such as Schiff base ligands, that can be sterically and electronically modified with ease are very attractive [1]. Recently, Kleij reported detailed knowledge of metal–salen complexes (metal: Cr, Co, Al, Zn, Cu, Mn, Sn, Ru) as catalysts for the coupling of epoxides with CO_2 [14]. To the best of our knowledge, Schiff bases containing Pd(II) as the metal centre have not been used as catalysts for chemical fixation of carbon dioxide [15]. In this study, six Pd(II) salen complexes (five of them are novel) have been synthesized and investigated as catalysts for the chemical coupling of CO_2 with epoxides.

2. Experimental

2.1. Materials and measurements

All reagents and solvents were of reagent grade quality and obtained from commercial suppliers (Aldrich or Merck). IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer

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as KBr pellets. ^{1}H NMR spectra were recorded on a Varian AS-400 MHz instrument in $CDCl_3$ at room temperature. Chemical shifts are given in parts per million from tetramethylsilane. Electronic spectral studies were recorded by an Analytic Jena Speedcord S-600 diod-array spectrophotometer. Melting points were measured in open capillary tubes with an Electrothermal 9100 melting point apparatus, and are uncorrected. The electrochemical properties of the palladium complexes were investigated by cyclic voltammetry (CV). The cyclic voltammetry measurements were recorded using a CH 660B model potentiostat from CH Instruments. The working electrode consisted of a glassy carbon electrode that was polished before the experiments. A platinum wire was used as a counter electrode. A silver wire served as a quasi-reference electrode. Measurements were carried out in 0.1 M $TBAPF_6$ as a supporting electrolyte in acetonitrile. All solutions in the cell were purged with argon before the measurements were taken. The sweep rate was kept constant at 0.1 V/s. The oxidation potential of the ferrocene/ferrocenium couple at about +0.45 V was used as an internal reference. Catalytic tests were performed in a PARR 4843 50 mL stainless pressure reactor.

*2.2. Synthesis of the ligands, **1–6***

The previously reported salen type ligands 1–5 [1–3,5,6,8,7] and the novel ligand **6** have been prepared from aliphatic diamines (ethylenediamine, 1,3-propanediamine and 2,2-dimethyl-1,3-propanediamine) with substituted salicylaldehydes in the presence of alcoholic media (ethyl or methyl alcohol) in high yields.

2.2.1. Synthesis of N,N′-bis(4-diethylaminosalicylidene)-2,2-dimethyl-propanediamine, 6

A mixture of 4-diethylaminosalicylaldehyde (2.0 mmoL), ethanol (20 mL) and 2,2-dimethyl-propanediamine (1.0 mmoL) was stirred for 12 h at room temperature. Also, 3–4 drops of formic acid were added as a catalyst. The resulting solution was concentrated in vacuum. The oily product was crystallized by layering a saturated CH_2Cl_2 solution with hexane (1:3). The desired ligand is soluble in common solvents such as $CHCl_3$, CH_3CH_2OH, DMF and DMSO. M.p.: 103–105 °C. Yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.03 (s, 6H, >C-(CH_3)$_2$); 1.18 (t, *J* = 7.2, 12H, -N-CH_2-CH_3); 3.37 (q, *J* = 7.7, 8H, -N-CH_2-CH_3); 6.16 (t, *J* = 5.2, 2H, *m*-aryl-*H*); 6.25 (dd, 2H, *m*-aryl-*H*); 6.99 (d, *J* = 8.8, 2H, *o*-aryl-*H*); 7.96 (s, 2H, N=C*H*); 13.65 (s, 2H, O*H*); ^{13}C NMR (100.56 MHz, $CDCl_3$, δ ppm): 166.9 (aryl-*C*-OH); 163.8 (N=*C*H); 151.9 (aryl-$C_{\text{(number-4)}}$-N); 133.1 (*o*-aryl-*C*); 108.4 (aryl-$C_{\text{(number-1)}}$); 103.3 (*m*-aryl-*C*); 98.5 (*m*-aryl-*C*); 65.7 (-*C*H_2-C-(CH_3)$_2$); 44.7 (-N-*C*H_2-CH_3); 36.5 (>*C*-(CH_3)$_2$); 24.2 (>C-(*C*H_3)$_2$); 12.9 (-N-CH_2-*C*H_3).

*2.3. Synthesis of the palladium(II) complexes **7–12***

The Pd(II) complex **7** was prepared according to the literature [10] by the reaction of an equivalent molar amount of the corresponding ligand with $Pd(OAc)_2$ in methanol.

2.3.1. Synthesis of N,N′-propylenebis(3,5-di-tert-butylsalicylaldiminato)palladium(II), 8

A hot methanolic solution of *N,N′*-bis(3,5-di-*tert*-butylsalicylidene)propanediamine (1 mmoL) and $Pd(OAc)_2$ (1 mmoL) were stirred for 5 h under an argon atmosphere. The precipitated yellow product was filtered via a cannula. It was then washed with a CH_2Cl_2:EtOH (1:3) mixture several times. M.p.: >300 °C. Yield: 72%. The NMR data could not be obtained because of the low solubility of the product, even with chloroform-d, acetone-d_6, dimethyl sulfoxide-d_6 and *N,N*-dimethylformamide-d_7 as the NMR solvent. *Anal.* Calc. for $C_{33}H_{48}N_2O_2Pd$ (MW: 611 g/mol): C, 64.85; H, 7.92; N, 4.58. Found: C, 65.08; H, 7.38; N, 4.27%.

2.3.2. Synthesis of N,N'-2,2-dimethylpropylenebis(3,5-di-tert-butylsalicylaldiminato)palladium(II), 9

The synthetic procedure was analogous to that used for **8**. The precipitated crude product was filtered via a cannula, washed with hot methanol twice and then dried under vacuo. The product was recrystallized from CH_2Cl_2-hexane. M.p.:>300 °C. Yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.08 (s, 6H, >C-(CH_3)$_2$); 1.26 (s, 18H, aryl-$C_{\text{(number-5)}}$-(CH_3)$_3$); 1.49 (s, 18H, aryl-$C_{\text{(number-3)}}$-(CH_3)$_3$); 3.36 (s, 4H, -CH_2-C-(CH_3)$_2$); 6.9 (s, 2H, *o*-aryl-*H*); 7.4 (d, *J* = 2.4, *p*-aryl-*H*); 7.57 (s, 2H, N=C*H*); ^{13}C NMR (100.56 MHz, $CDCl_3$, δ ppm): 164.3 (N=*C*H); 163.3 (aryl-*C*-OH); 139.9 (aryl-$C_{\text{(number-5)}}$-(CH_3)$_3$); 135.9 (aryl-$C_{\text{(number-3)}}$-(CH_3)$_3$); 130.5(*o*-aryl-*C*); 127.9 (*p*-aryl-*C*); 118.9 (aryl-$C_{\text{(number-1)}}$); 71.9 (-*C*H_2-C-(CH_3)$_2$); 36.1 (*C*-(CH_3)$_3$); 33.9 (C-(*C*H_3)$_3$); 31.5 (C-(*C*H_3)$_3$); 30.1 (>*C*-(CH_3)$_2$); 24.5 (>C-(*C*H_3)$_2$). *Anal.* Calc. for $C_{35}H_{52}N_2O_2Pd$ (MW: 639 g/mol): C, 65.76; H, 8.20; N, 4.38. Found: C, 65.43; H, 8.13; N, 4.01%.

2.3.3. Synthesis of N,N′-ethylenebis(4-diethlyaminosalicylaldiminato)palladium(II), 10

The synthetic procedure was analogous to that used for **9**. M.p.: 275 °C (dec.). Yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.10 (t, *J* = 7.2, 12H, -N-CH_2-CH_3); 3.27 (q, *J* = 6.4, 8H, -N-CH_2-CH_3); 3.55 (s, 4H, -N-CH_2-CH_2-N); 5.96 (d, *J* = 6.4, 2H, *o*-aryl-*H*); 6.31 (s, 2H, *m*-aryl-*H*); 6.84 (d, *J* = 8.4, 2H, *m*-aryl-*H*); 7.26 (s, 2H, N=C*H*); ^{13}C NMR (100.56 MHz, $CDCl_3$, δ ppm): 167.3 (N=*C*H); 157.0 (aryl-*C*-OH); 135.5 (aryl-$C_{\text{(number-4)}}$-N); 112.1 (*o*-aryl-*C*); 102.6 (aryl-$C_{\text{(number-1)}}$); 101.0 (*m*-aryl-*C*); 59.7 (-*C*H_2-*C*H_2); 46.7 (-N-*C*H_2-CH_3); 13.1 (-N-CH_2-*C*H_3). *Anal.* Calc. for $C_{24}H_{32}N_4O_2Pd$ (MW: 515 g/mol): C, 55.98; H, 6.26; N, 10.88. Found: C, 56.21; H, 6.95; N, 9.98%.

2.3.4. Synthesis of N,N′-propylenebis(4-diethlyaminosalicylaldiminato)palladium(II), 11

The synthetic procedure was analogous to that used for **9**. M.p.: 193 °C (dec.). Yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.08–1.12 (m, 12H, -N-CH_2-CH_3); 3.34–3.40 (m, 14H, -N-CH_2-CH_3, N-CH_2-CH_2-CH_2-N); 5.89 (d, *J* = 8.0, 2H, *m*-aryl-*H*); 6.25 (dd, 2H, *m*-aryl-*H*); 7.24 (dd, 2H, *o*-aryl-*H*); 7.71 (s, 1H, N=C*H*); 7.78 (s, 1H, N=C*H*); ^{13}C NMR (100.56 MHz, $CDCl_3$, δ ppm): 165.9 (N=*C*H); 160.2 (aryl-*C*-OH); 153.1 (aryl-$C_{\text{(number-4)}}$-N); 135.7 (*o*-aryl-*C*); 111.3 (aryl-$C_{\text{(number-1)}}$); 102.7 (*m*-aryl-*C*); 99.1 (*m*-aryl-*C*); 60.2 (*C*H_2-CH_2-*C*H_2); 55.3 (-N-*C*H_2-CH_3); 44.9 (CH_2-*C*H_2-CH_2); 13.1 (-N-CH_2-*C*H_3). *Anal.* Calcd. for $C_{25}H_{34}N_4O_2Pd$ (MW: 529 g/mol): C, 56.76; H, 6.48; N, 10.59. Found: C, 57.11; H, 6.81; N, 9.66%.

2.3.5. Synthesis of N,N′-2,2-dimethylpropylenebis(4-diethlyaminosalicylaldiminato)palladium(II), 12

The synthetic procedure was analogous to that used for **8**. M.p.: 278 °C (dec.). Yield: 81%. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 0.94 (s, 6H, >C-(CH_3)$_2$); 1.09 (t, *J* = 7.0, 12H, -N-CH_2-CH_3); 3.19 (s, 4H, -CH_2-C-(CH_3)$_2$); 3.26 (q, *J* = 7.2, 8H, -N-CH_2-CH_3); 5.94 (d, *J* = 8.0, 2H, *o*-aryl-*H*); 6.22 (s, 2H, *m*-aryl-*H*); 6.83 (d, *J* = 9.2, 2H, *m*-aryl-*H*); 7.14 (s, 2H, N=C*H*); ^{13}C NMR (100.56 MHz, $CDCl_3$, δ ppm): 166.7 (N=CH); 160.5 (aryl-*C*-OH); 153.5 (aryl-$C_{\text{(number-4)}}$-N); 135.4 (*o*-aryl-*C*); 110.9 (aryl-$C_{\text{(number-1)}}$); 102.6 (*m*-aryl-*C*); 99.8 (*m*-aryl-*C*); 71.9 (-*C*H_2-C-(CH_3)$_2$); 44.6 (-N-*C*H_2-CH_3); 34.3 (>*C*-(CH_3)$_2$); 24.2 (-N-CH_2-*C*H_3); 13.1 (>C-(*C*H_3)$_2$). *Anal.* Calc. for $C_{27}H_{35}N_4O_2Pd$ (MW: 529 g/mol): C, 56.76; H, 6.48; N, 10.59. Found: C, 57.11; H, 6.81; N, 9.66%.

2.4. General procedure for the cycloaddition of epoxides to CO_2

A stainless pressure reactor (50 mL) was charged with complex **7–12** (4.5×10^{-5} moL), epoxide (4.5×10^{-3} moL), DMAP (11 mg, 9.0×10^{-5} moL) and CH_2Cl_2 (5.0 mL). The reaction vessel was placed under a constant pressure of carbon dioxide for 2 min to allow the system to equilibrate and CO_2 was charged into the autoclave to the desired pressure, then the autoclave was heated to the desired temperature. The pressure was kept constant during the reaction. The vessel was allowed to cool in an ice bath after the expiration of the desired reaction time. The pressure was released, and then the excess gases were vented. The yields of epoxides to corresponding cyclic carbonates were determined by comparing the ratio of product to substrate in the ^1H NMR spectrum of an aliquot of the reaction mixture.

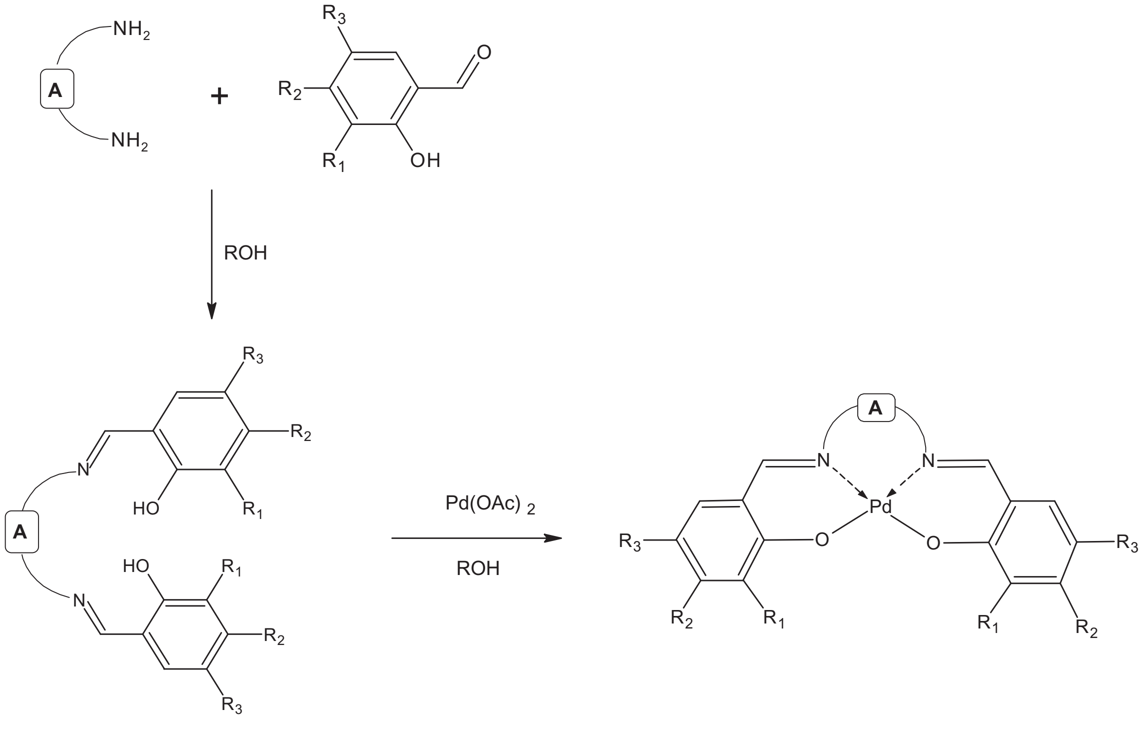
2.5. X-ray crystallography

An X-ray quality yellow crystal of **9** was obtained via layering a saturated CH_2Cl_2 solution with hexane. A crystal of **9** suitable for data collection was mounted on a glass fibre and data collection was performed on a STOE IPDS II diffractometer with graphite monochromated Mo $K\alpha$ radiation at 296 K. The structure was solved by direct-methods using SHELXS-97 [16] and refined by full-matrix least-squares methods on F^2 using SHELXL-97 [17] from within the WINGX [18,19] suite of software. All non-hydrogen atoms were refined with anisotropic parameters. Hydrogen atoms bonded to carbon were placed in calculated positions (C–H = 0.93–0.97 Å) and treated using a riding model with U = 1.2 times the U value of the parent atom for CH, CH_2 and CH_3. Molecular diagrams were created using ORTEP-III [20]. Geometric calculations were performed with PLATON [21]. The unit cell has an accessible solvent volume of 2830 Å^3 which is occupied by a severely disordered dichloromethane molecule. Therefore, this molecule was eliminated from the refinement of the structure by means of the SQUEEZE subroutine of PLATON [21] and the hkl intensities were modified accordingly.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic route used for the preparation of the salen-functionalized palladium(II) complexes **7–12** is shown in Scheme 1. The Schiff bases **1–5** [9–15] and **6** were prepared by condensation of 3,5-di-*t*-butylsalicylaldehyde [13] or 4-diethylamino salicylaldehyde with commercially available aliphatic diamines (ethylenediamine, 1,3-propanediamine and 2,2-dimethyl-1,3-propanediamine). The salen ligands were isolated and then washed with methanol to remove traces of the reactants. The Pd(II) complex **7** was prepared according to the literature [10] by the reaction of a molar equivalent of ligand **1** with $Pd(OAc)_2$ in methanol. The



1 - 6

7 - 12

Schiff Bases

Compound	R_1	R_2	R_3	A
1	^tBu	H	^tBu	$-CH_2CH_2-$
2	^tBu	H	^tBu	$-CH_2CH_2CH_2-$
3	^tBu	H	^tBu	$-CH_2C(CH_3)_2CH_2-$
4	H	NEt_2	H	$-CH_2CH_2-$
5	H	NEt_2	H	$-CH_2CH_2CH_2-$
6	H	NEt_2	H	$-CH_2C(CH_3)_2CH_2-$

Pd(II) complexes

Compound	R_1	R_2	R_3	A
7	^tBu	H	^tBu	$-CH_2CH_2-$
8	^tBu	H	^tBu	$-CH_2CH_2CH_2-$
9	^tBu	H	^tBu	$-CH_2C(CH_3)_2CH_2-$
10	H	NEt_2	H	$-CH_2CH_2-$
11	H	NEt_2	H	$-CH_2CH_2CH_2-$
12	H	NEt_2	H	$-CH_2C(CH_3)_2CH_2-$

Scheme 1. Synthetic route to the salen–Pd(II) complexes.

Table 1
Characteristic IR bands (cm^{-1}) of the synthesized compounds as KBr pellets.

	Compounds											
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
ν(O–H)	3419	3390	3428	3436	3435	3461	–	–	–	–	–	–
ν(C=N)	1631	1633	1633	1634	1618	1618	1626	1609	1614	1590	1584	1589

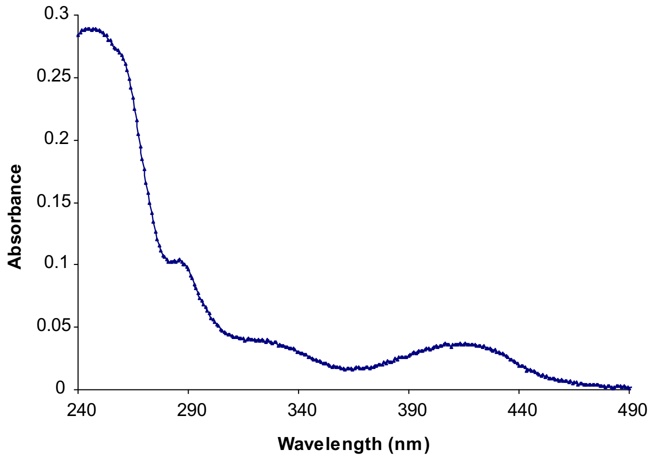


Fig. 1. UV–Vis absorption spectra of the palladium complex **9** in dichloromethane solvent.

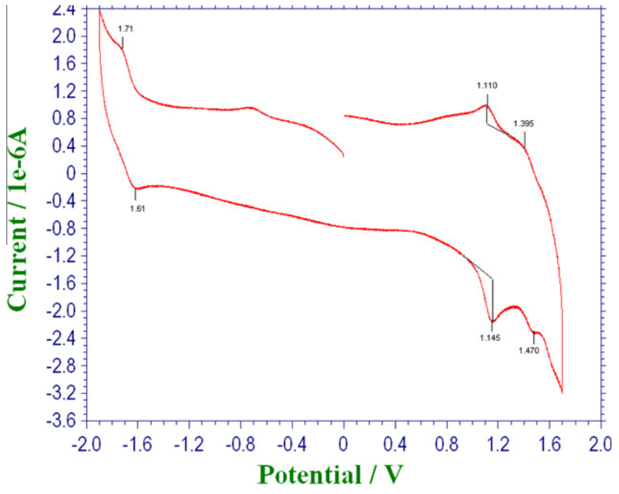


Fig. 2. Cyclic voltammograms at a glassy carbon electrode for complex **9** (1 mM) in MeCN containing 100 mM [TBA][PF6].

other Pd(II) salen complexes were synthesized in a similar manner. The obtained crude products were purified by re-crystallization from CH_2Cl_2/MeOH (3:10) at 25 °C. The compounds were obtained as pale yellow crystals.

Table 3
Crystal data and structure refinement parameters for **9**.

Empirical formula	$C_{35}H_{52}N_2O_2Pd$
Formula weight	639.19
T (K)	296
λ (Å)	0.71073
Crystal system	monoclinic
Space group	$C2/c$
Unit cell dimensions	
a (Å)	23.6808(18)
b (Å)	31.743(3)
c (Å)	14.5164(13)
α (°)	90
β (°)	125.795(6)
γ (°)	90
V (Å^3)	8850.7(14)
Z	8
D_{calc} (mg/m^{-3})	0.959
Absorption coefficient (mm^{-1})	0.44
F(000)	2704
Crystal size (mm)	0.48 × 0.32 × 0.07
θ Range for data collection (°)	1.2–26.8
Independent reflection	8695
Collected reflection	56348
Absorption correction	integration
T_{min}	0.522
T_{max}	0.958
R_{int}	0.099
θ_{max}(°)	26
h	$-29 \rightarrow 29$
k	$-39 \rightarrow 39$
l	$-17 \rightarrow 17$
Refinement method	Full-matrix least-squares on F^2
Final R indices [$I > 2\sigma(I)$]	0.049
$wR(F^2)$	0.093
Goodness-of-fit on F^2	0.98
$(\Delta/\sigma)_{max}$	0.001
$\Delta\rho_{max}$ (e Å^{-3})	0.32
$\Delta\rho_{min}$ (e Å^{-3})	−0.56

All the synthesized compounds **1–12** were fully characterized by ^1H and ^{13}C NMR spectroscopy. In the ^{1}HNMR spectra of the ligands, obtained in $CDCl_3$, singlet peaks appear at around 8 ppm, which were assigned to the protons of azomethine [22]. The ^{1}H NMR ($CDCl_3$) spectra of the ligands show proton signals at *ca* 1 ppm, indicating the presence of the ^{t}Bu substituents on the aryl rings of the salt at position 3 and 5, indicating that the ^{t}Bu protons of these compounds are magnetically non-equivalent [23]. Also, the elemental analysis results of the Pd(II) complexes are in agreement with the proposed structure, as shown in Scheme 1. Details of the synthesis and product characterization are given in the experimental section.

Table 2
Molecular orbital energies of complex 9 with respect to the vacuum level.

	E^0_{red} (V)	E^0_{ox1} (V)	E^0_{ox2}(V)/E^0_{ox3}(V)	LUMO (eV)	HOMO (eV)	E_g (eV)
Complex **9**	−1.6	1.11	1.39	−2.72	−5.48	2.76

HOMO and LUMO energy levels of complex **9** were determined by the formulae:
$E_{LUMO} = -(4.8 + E_{red}^{onset})$, $E_{red}^{onset} = E°_{red} - E°_{ox(ferrocene)}$, $E_{HOMO} = E_{LUMO} - E_{gap}$.

The IR spectra of the salen ligands showed peaks in the νC=N stretching frequency region at 1634–1618 cm^{-1}. The bands at 3461–3419 cm^{-1} are due to the O-H group of the salicylaldimine units, as given in Table 1. The IR spectra of the palladium complexes **7–12** showed that the C=N stretching band shifted by *ca* 5–44 cm^{-1} to lower frequency, compared to the salts as shown Table 1. This is due to the effect of the metal on the ligand system [12].

UV–Vis absorption spectra of the Pd complexes taken in dichloromethane solution are shown in Fig. 1. The spectra of the Pd(II) complexes were recorded in the 200–800 nm range in CH_2Cl_2 solution. As given in Fig. 1, the electronic spectra of the Pd(II) complexes in CH_2Cl_2 showed absorption bands in the 200–500 nm range, exhibiting two absorption bands at 230–280 and 360–450 nm. The bands in the region 230–280 nm are attributed to π– π^* transitions of the aromatic ring of the ligands. The bands in the region 360–450 are nm due to the n–π^* transition of the non-bonding electrons present on the nitrogen of the azomethine (C,N) groups in the ligands. While complex **8** has absorption peaks at 256 and 412 nm, complex **9** has absorption peaks at 249 and 419 nm. Both **8** and **9** exhibit almost the same absorption properties in the UV–visible spectrum in the 200–500 nm range. These complexes have conjugated π electron system interactions between the Pd metal and the aromatic ligand, which can be attributed to the charge transfer bands (metal to ligand or ligand to metal). There is a small bathochromic shift (~7 nm) in electronic spectrum of complex **9** compared with complex **8**. It has been reported that absorption bands observed within the range 232–408 nm in CH_2Cl_2 are most probably due to π–π^* transitions in the aromatic benzene ring or n–π^* transitions of the imine group of the ligands [24].

The cyclic voltammogram of complex **9** is given in Fig. 2. This complex compound shows reversible reduction and oxidation. A reversible reduction wave showing an electron process was observed in the range 1.61/1.71 V for compound **9**, and it exhibited two or three anodic waves with the corresponding cathodic waves and one cathodic wave with the corresponding anodic waves, indicating a reversible process. The anodic wave showing the first oxidation is assigned a ligand-based oxidation. The anodic peak potentials of the complex were located in the 1.6–1.8 V range. The measured redox potentials and energies of the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbials (LUMO) of the complex are listed in Table 2. In order to calculate the LUMO energy level of the complex with respect to the vacuum level, the redox data are standardized to the ferrocene/ferricenium couple, which has a calculated absolute energy of -4.8 eV [25]. Taking the reduction onsets into account, the LUMO energy levels have been calculated and listed in Table 1. The HOMO energy levels of complex **9**, containing aromatic rings, are calculated to be about −5.53 and −5.48 eV. The corresponding LUMO energy levels are found to be −2.72 eV, using the formula $E_{HOMO} = E_{LUMO} - E_{gap}$. The optical band gap value (E_g) was calculated as 2.76 eV.

Table 4
Selected bond lengths (Å) and angles (°) for **9**.

N1–Pd1	1.984(3)	O1–Pd1	2.012(2)
N2–Pd1	1.994(3)	O2–Pd1	1.993(3)
N1–Pd1–O2	172.78(11)	N1–Pd1–O1	92.01(11)
N1–Pd1–N2	94.55(12)	O2–Pd1–O1	82.11(11)
O2–Pd1–N2	91.56(12)	N2–Pd1–O1	172.75(11)

3.2. Crystallography

Important crystallographic data and the structure refinement details of **9** are listed in Table 3, selected bond lengths and bond angles are summarized in Table 4, and its ORTEP view is shown in Fig. 3. The Pd(II) ion has a distorted square–planar environment, in which the ligand is coordinated to the Pd(II) ion as a tetradentate chelating ligand via the two phenolic oxygen atoms and two imine nitrogen atoms, yielding three six-membered rings. The two rings (Pd1/N1/C15/C6/C1/O1 and Pd1/N2/C35/C26/C21/O2) are essentially planar and the third (Pd1/N1/C16/C17/C18/N2) adopts a half-chair conformation, with the atom C17 displaced from the Pd1/N1/C16/C18/N2 plane by 0.454(5) Å and with Cremer and Pople (1975) puckering parameters [26]: $Q = 0.594(4)$ Å, $\theta = 59.3(4)°$ and $\varphi = 186.4(5)°$. The Pd(II) complex is coordinated in a cis-planar fashion by the two phenolic oxygen atoms and two imine nitrogen atoms. The Pd–O distances are 1.993(3)–2.012(2) Å with Pd–N distances 1.984(3)–1.994(3) Å, which are typical for square–planar Pd(II) complexes of Schiff base ligands [27]. The bond angles around the Pd(II) ion indicate that the complex has a distorted square-planar geometry, O–Pd–O angle

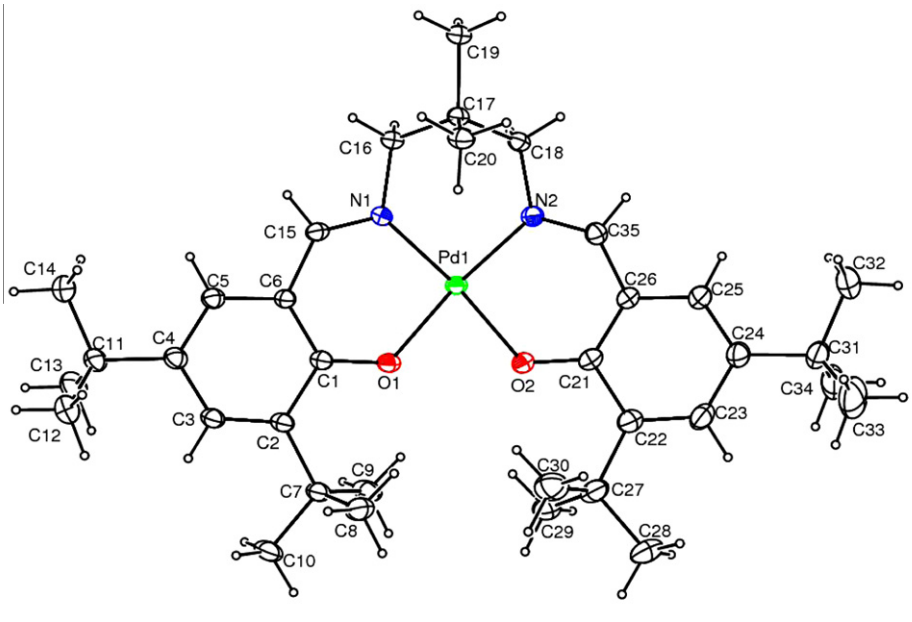


Fig. 3. The molecular structure of **9**. Displacement ellipsoids are drawn at the 30% probability level.

Table 5
Hydrogen bonds and C–H···π interactions for **9**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
C8–H8B···O1	0.96	2.40	3.041(5)	124
C9–H9A···O1	0.96	2.36	3.000(4)	124
C29–H29B···O2	0.96	2.35	2.986(5)	123
C30–H30A···O2	0.96	2.38	3.010(6)	123
X···H(I)	Cg(J)	H···Cg (Å)	X–H···Cg (°)	
C(16)–H(16B)	Cg(5)$^{\text{i}}$	3.3169	137.69	
C(19)–H(19A)	Cg(4)$^{\text{ii}}$	2.9502	166.41	

Cg(4): C1–C2–C3–C4–C5–C6, Cg(5): C21–C22–C23–C24–C25–C26.
Symmetry codes: (i) 3/2 − *x*, 1/2 − *y*, 1 − *z*; (ii) 1 − *x*, *y*, 1/2 − *z*.

82.11(11)° and N–Pd–N angle 94.55(12)°, deviating substantially from that expected for a regular square–planar geometry. The distortion can be attributed to the restricted bite angle of the Schiff base ligand. Other bond lengths and angles observed in the structure are normal [28]. The two phenolate rings, (C1–C6) and (C21–C26), are planar, the maximum deviations from the least-squares planes being 0.0113(29) Å for atom C4 and 0.0214(33) Å for atom C22. The dihedral angle between the two phenolate rings of the tetradentate Schiff base ligand is 12.8(3)°.

Within the selected asymmetric unit, intramolecular C–H···O hydrogen bonds define S(6) motifs. Compound 9 also contains two intermolecular C–H···π interactions. In the first, atom C16 in the molecule at (*x*, *y*, *z*) acts as hydrogen-bond donor to the C21–C26 benzene ring in the molecule at (3/2 − *x*, 1/2 − *y*, 1 − *z*), so forming a centrosymmetric $R_2^2(14)$ ring. In the second, atom C19 in the molecule at (*x*, *y*, *z*) acts as hydrogen-bond donor to the C1–C6 benzene ring in the molecule at (1 − *x*, *y*, 1/2 − *z*), so forming a centrosymmetric $R_2^2(16)$ ring. Details of these interactions are given in Table 5. The combination of the C–H···π interactions form a chain running parallel to the [1 0 0] direction, as shown in Fig. 4.

3.3. Catalytic studies

The cycloaddition reaction of carbon dioxide with epoxides in the presence of 1% 7–12 was conducted as a model reaction for testing the use of these complexes as catalysts, and the results are compiled in Table 6. It is clear from Table 6 that bonding species to the metal centre is influencing the yield of the cyclic carbonate (entries 1–12). Epichlorohydrin (EC) was found to be the most reactive epoxide, while propylene oxide (PO) exhibited low activity [29].

The salen Pd(II) complexes all showed catalytic efficiency only while using EC as the substrate (Table 6, entries 7–12, 14). With the other epoxides, such as PO and epoxybutane (EB), these complexes did not show the desired activity. On increasing the catalyst

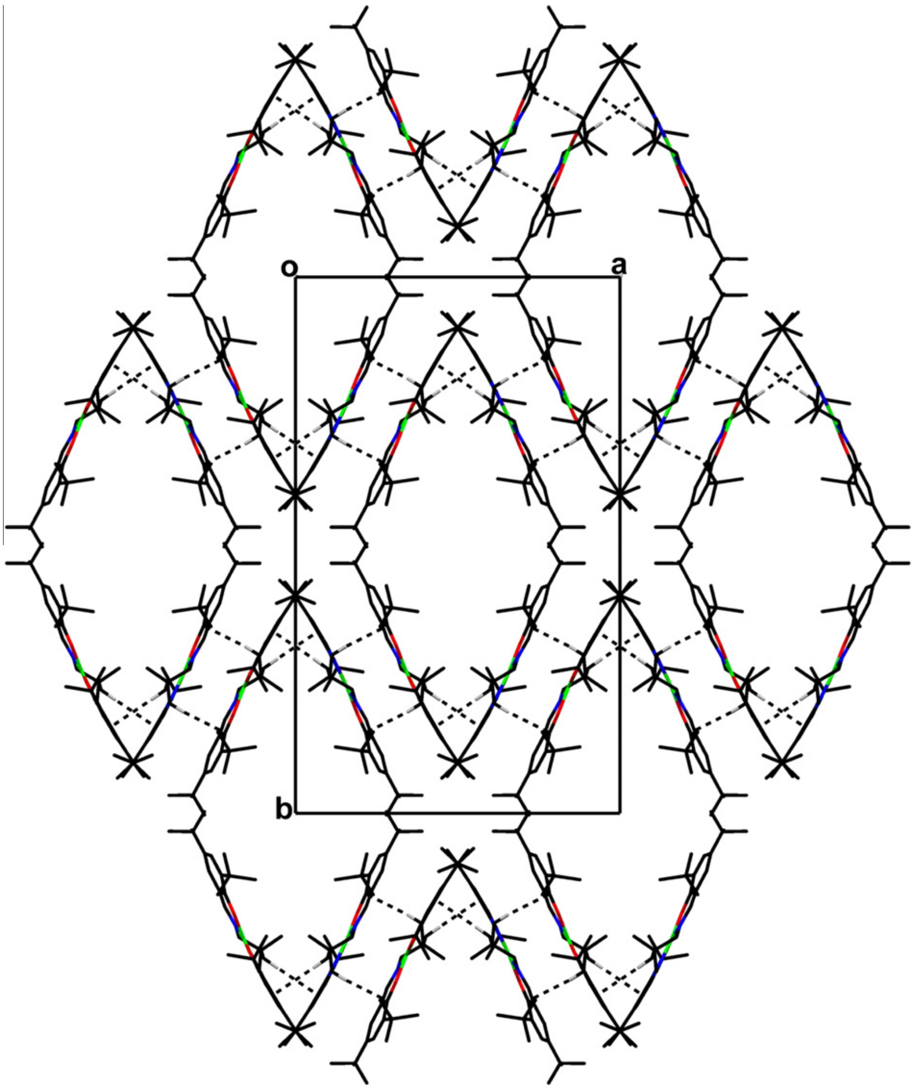
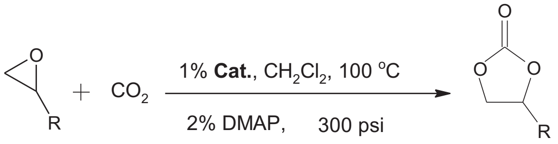
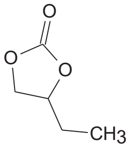
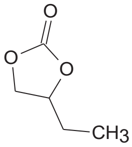
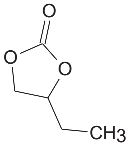
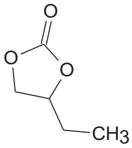
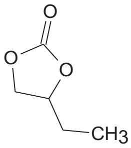
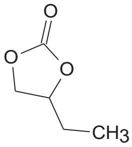
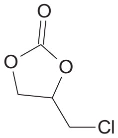
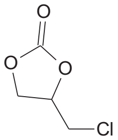
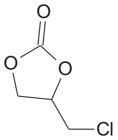
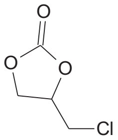
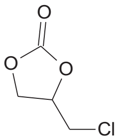
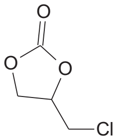
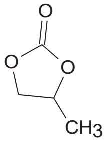
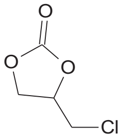
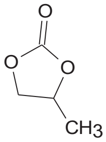


Fig. 4. Packing arrangement of the molecules in the unit cell.

Table 6
R = Propylene oxide (PO), epichlorohydrine (EC), and 1,2-epoxy butane (EB)



Entries	Catalyst	Product	Yield (%)[a]	TOF[b]
1	**7**		27.5	13.8
2	**8**		17.2	8.6
3	**9**		12.8	6.4
4	**10**		13.5	6.8
5	**11**		27.0	13.5
6	**12**		28.3	14.2
7	**7**		92.0	46.0
8	**8**		97.5	48.8
9	**9**		96.6	48.3
10	**10**		96.3	48.2
11	**11**		93.2	46.6
12	**12**		87.7	43.9
13	**12**		23.4	11.7
14	**12**		82.4[c]	412
15	–		5.0[d]	25.0

[a] Yield of epoxides to the corresponding cyclic carbonates was determined by comparing the ratio of product to substrate in the ^1H NMR spectrum of an aliquot of the reaction mixture.
[b] The rate is expressed in terms of the turnover frequency (TOF (mol of product (mol of catalyst h)$^{-1}$) = turnovers/h).
[c] (4.5×10^{-5} mol) complex **12** as catalyst, and epichlorohydrine (4.5×10^{-2} mol) was used as substrate.
[d] Blank run, without any Pd(II) complex as a catalyst.

loading to 1%, a high conversion (TON = 824) was obtained while using catalyst **12** and EC as the substrate (Table 6, entry14).

According to the catalytic results, the more electron donating substituents on the backbone and the aryl ring of the ligand system, in particular, effectively promote carbon dioxide activation with liquid epoxides under homogeneous conditions.

4. Conclusion

Salen type Pd(II) complexes (**7**–**12**) have been synthesized and spectroscopically characterized. The structure of complex **9** has been confirmed by X-ray analysis. These Pd(II) complexes were used as catalysts for the formation of cyclic organic carbonates from carbon dioxide and liquid epoxides, which served as both reactant and solvent. The salen Pd(II) complexes all showed catalytic efficiency when using EC as the substrate.

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