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Synthesis, characterization, redox behavior and hydrogenation catalytic activity of bis(*N*-aryl-3, 5-Bu$^t_2$-salicylaldiminato)palladium(II) complexes

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Abstract

The synthesis, spectroscopic (^{1}H NMR, IR, UV–Vis), electron-transfer properties and catalytic reactivity of new palladium(II) complexes with *N*-aryl-3, 5-Bu$^t_2$-salicylaldimines prepared from 3, 5-Bu$^t_2$-salicylaldehyde and *o*-,*p*-substituted anilines (X–$C_6H_4NH_2$, X = H, F, Cl, Br, CH_3, OCH_3, *t*-Bu, 5,6-benzo) are reported. Cyclic voltammetry studies of the complexes exhibit an irreversible anodic peak that corresponds to the phenoxide/phenoxyl oxidation. The chemical oxidation of the complexes with $(NH_4)_2Ce(NO_3)_6$ in $CHCl_3$, besides relatively stable Pd^{II}–phenoxyl radical complexes (g = 2.0083–2.0114), also generate nitroxide radicals exhibiting strongly anisotropic spectra ($g_\parallel$ = 2.0061, $g_\perp$ = 2.0072, $A_\parallel$ = 37.5, $A_\perp$ = 5.38 G) typical for immobilized nitroxide radicals. It has been found that the introduction of *t*-Bu groups on the salicylic ring increases catalytic activity of towards hydrogenation of nitrobenzene in DMF at room temperature.

Keywords: *N*-Aryl-3, 5-Bu$^t_2$-salicylaldiminepalladium(II) complexes; Spectroscopy; Electrochemistry; Pd(II)–phenoxyl radicals; Nitroxide radicals; Catalytic hydrogenation

1. Introduction

The design, synthesis and structural characterization of salicylaldimine complexes is a subject of current interest due to their interesting structural, magnetic, spectral, catalytic and redox properties, use as models for enzymes and various theoretical interest [1–4]. Our interest in these compounds was associated with the structure, electron-transfer and catalytic reactivity of the *N*-aryl-salicylaldimine transition metal(II) chelates bearing redox-active Bu$^t_2$ functionalized aminophenolic and aniline frames [5,6,7a,8a,8d]. While upon oxidation they easily generate M(II)-phenoxyl radical complexes [5,6], the proceeding unexpected oxidative C–C coupling in Cu^{II} complexes [5b] and reduction via radical intermediates of Cu^{II} and Pd^{II} bis-salicylaldiminates upon treatment with PPh_3 were also observed [6].

In our previous work, we were interested in how the bulky Bu^t groups would affect the electron-transfer reactivity of this family of complexes if they were introduced on the salicylaldehyde ring [6d,7a,8a]. It should be noted that while the chemistry of metal complexes with salen-type and other polydentate ligands bearing 2, 4-Bu$^t_2$-phenyl moieties has been extensively studied because of their efficient catalytic activity and their use as model complexes for metalloproteins having metal centers and proximal organic radicals in their active site

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[4,7], there has been comparatively little work reported on the metal complexes with bidentate *N*-aryl-3, 5-Bu^t_2-salicylaldimines derived from 3, 5-Bu^t_2-salicylaldehyde (3,5-DTBS) [4c,6d,8].

In the present work, the synthesis, spectroscopy, chemical and electrochemical oxidation as well as reactivity in the hydrogenation of $PhNO_2$, of palladium(II) complexes with *N*-aryl-3, 5-Bu^t_2-salicylaldimines (L^xH) derived from 3,5-DTBS and substituted anilines (X–$C_6H_4NH_2$, where X = H, *o*,*p*-F, Cl, Br, CH_3, OCH_3, *p*-Bu^t and 5,6-benzo) are reported.

2. Experimental

2.1. Materials and equipment

All solvents, aniline derivatives, 2,4-di-*t*-butylphenol, hexamethylenetetramine, nitrobenzene, acetic acid, $(NH_4)_2Ce(NO_3)_6$ and $Pd(ac)_2$ were of reagent grade (Aldrich) and were used without further purification. 3, 5-Bu^t_2-salicylaldehyde was prepared from commercially available 2,4-di-*t*-butyl-phenol according to the literature [9]. Elemental analyses (C, H, N) and spectroscopic (IR, UV–Vis, ^{1}H NMR, ESR) characterizations were made according to literature [8d,10]. Cyclic voltammetry (CV) measurements were made using Volta Lab PGZ 301 Dynamic Voltammetry under argon atmosphere. In this system a SCE (saturated calomel electrode) was used as a reference electrode (the ferrocene/ferrocenium couple oxidation was found to be 0.84 V versus SCE in DMF in our system). Platinum bead and platinum coil electrodes were employed as the working and the auxiliary electrodes, respectively. CV measurements were recorded in DMF and acetonitrile (MeCN) at 300 K, and $[n\text{-}(C_4H_9)_4]BF_4$ was used as a supporting electrolyte. The concentration of the complexes was about 0.001 M for each measurement. The voltage scan rate during the CV measurements was 100 mV/s (see Table 4).

2.2. Preparation of the ligands

The ligands were *N*-phenyl-3, 5-Bu^t_2-salicylaldimine (L^1H), *N*-2-F-phenyl-3, 5-Bu^t_2-salicylaldimine (L^2H), *N*-4-F-phenyl-3, 5-Bu^t_2-salicylaldimine (L^3H), *N*-2-Cl-phenyl-3, 5-Bu^t_2-salicylaldimine (L^4H), *N*-4-Cl-phenyl-3, 5-Bu^t_2-salicylaldimine (L^5H), *N*-2-Br-phenyl-3, 5-Bu^t_2-salicylaldimine (L^6H), *N*-4-Br-phenyl-3, 5-Bu^t_2-salicyla-]ldimine (L^7H) *N*-2-CH_3-phenyl-3, 5-Bu^t_2-salicylaldimine (L^8H), *N*-4-CH_3-phenyl-3, 5-Bu^t_2-salicylaldimine (L^9H), *N*-2-OCH_3-phenyl-3, 5-Bu^t_2-salicylaldimine ($L^{10}H$), *N*-4-OCH_3-phenyl-3, 5-Bu^t_2-salicylaldimine ($L^{11}H$), *N*-4-Bu^t-phenyl-3, 5-Bu^t_2-salicylaldimine ($L^{12}H$) and *N*-5, 6-benzo-3, 5-Bu^t_2-salicylaldimine ($L^{13}H$). Their complexes were abbreviated as **1**, **2**, **3**, **4**, **5**, **6**, **7**, **8**, **9**, **10**, **11**, **12** and **13**, respectively. The ligands were synthesized by refluxing in the methanol the aniline derivatives with 3,5-DTBS in a 1:1 molar ratio as recently described [8d].

2.3. Preparation of complexes

Palladium(II) acetate (0.125 g, 0.5 mmol) was added as a solid to a stirring warm solution of L^xH (1 mmol) in absolute methanol (40 ml). The resulting mixture was heated with stirring at ca. 40–45 °C on a water bath for about 30–40 min. Then the volume of the solution was reduced to 10–15 ml by slow evaporation at room temperature. The precipitated solid was collected by filtration and washed with water and then with 2–3 ml cooled MeOH, dried in air and recrystallized from acetonitrile–$CHCl_3$ mixture (5:1). Some physico-chemical characteristics are given in Table 1. For comparative purposes in the catalytic activity studies, bis(*N*-4-CH_3Ph-salicylaldiminato)Pd(II) was also prepared.

Table 1
Physico-chemical and analytical data for complexes **1**–**13**

Compound	M.p. (°C)	Yield (%)	Formula	Found (calcd.) (%)		
				C	H	N
1	>270	47	$C_{42}H_{52}N_2O_2Pd$	70.56 (69.84)	7.69 (7.25)	3.43 (3.87)
2	>260	36	$C_{42}H_{50}N_2O_2F_2Pd$	67.23 (66.53)	6.46 (6.64)	3.78 (3.69)
3	>260	37	$C_{42}H_{50}N_2O_2F_2Pd$	66.23 (66.53)	6.34 (6.64)	3.94 (3.69)
4	184	38	$C_{42}H_{50}N_2O_2Cl_2Pd$	64.13 (63.75)	6.87 (6.37)	3.09 (3.54)
5	180	45	$C_{42}H_{50}N_2O_2Cl_2Pd$	63.18 (63.75)	6.78 (6.37)	3.23 (3.54)
6	207	39	$C_{42}H_{50}N_2O_2Br_2Pd$	56.78 (57.18)	5.45 (5.71)	2.98 (3.17)
7	218	42	$C_{42}H_{50}N_2O_2Br_2Pd$	57.68 (57.18)	5.64 (5.71)	2.79 (3.17)
8	194	51	$C_{44}H_{56}N_2O_2Pd$	70.75 (70.34)	5.18 (5.51)	3.42 (3.73)
9	159	38	$C_{44}H_{56}N_2O_2Pd$	69.78 (70.34)	6.18 (5.51)	4.12 (3.73)
10	150[a]	46	$C_{44}H_{56}N_2O_4Pd$	67.68 (67.46)	6.89 (7.21)	3.11 (3.57)
11	205	35	$C_{44}H_{56}N_2O_4Pd$	68.15 (67.46)	7.36 (7.21)	3.32 (3.57)
12	265	43	$C_{50}H_{68}N_2O_4Pd$	72.23 (71.88)	7.86 (8.20)	3.68 (3.35)
13	>250[a]	49	$C_{52}H_{56}N_2O_4Pd$	73.31 (72.93)	7.12 (6.85)	3.56 (3.40)

[a] Decomposition.

2.4. Hydrogenation procedure

The hydrogenation of nitrobenzene was carried out in a thermostatic reaction flask (100 ml) at 25 °C under 760 Torr H_2 with vigorous stirring in dry and deoxygenated 25 ml DMF solution. Catalyst ($1.0–4.0 \times 10^{-5}$ mol) was added into 25 ml DMF and saturated with H_2 for 15–20 min. After addition of $NaBH_4$ (5×10^{-5} mol) the mixture was stirred for ca. 5 min and $PhNO_2$ ($4–8 \times 10^{-4}$ mol) was transferred into the vessel. Then the H_2 gas was bubbled again into the flask and the volume of the absorbed H_2 was measured periodically.

3. Results and discussion

Our preliminary examination revealed that the presented L^xH ligands easily coordinate Cu(II) [8d], unlike Ni(II), VO(II), Mn(II), Zn(II) and Cd(II). All of complexes **1**–**13** can be prepared under mild conditions, only with lower yields. The reason of this might be the stronger interligand steric hindrance caused by the 3-Bu^t group of the ligands, since the same complication did not occur during the complexion of salicylaldimines derived from non di-butylated salicylaldehydes and di-Bu^t anilines. When palladium(II) was prepared under refluxing conditions in MeOH, EtOH or CH_3COOH, a progressive decomposition of the formed complexes to Pd(0) takes place. The analytical data show that the complexes have a ligand-to-metal ratio of 2:1. All compounds are soluble in polar solvents such as $CHCl_3$, CH_2Cl_2, DMF and DMSO.

3.1. Spectroscopic characterization

The analytical, IR, electronic, ^1H and ^{13}C NMR spectroscopic characteristics of the ligands were described in a previous report [8d]. The disappearance of free ligand absorptions around 2500–2800 cm^{-1} and lower frequency shifts of ν(CH=N) in the IR spectra of complexes **1**–**12**, suggest chelating of L^xH via a deprotonated –OH group and azomethine nitrogen atom (Table 2). A strong band at about 1528 cm^{-1}, detected in the spectra of complexes **1**–**12**, is assigned to ν(C–O) of the coordinated salicylic C–O bond [11]. Surprisingly, the IR and electronic spectra of (**13**) are remarkably different from the other complexes (Table 2).

The electronic spectra of compounds **1**–**13** (Table 2) in $CHCl_3$ and DMF (Table 2) consist of very intense bands due to intraligand $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, and absorptions at 400–420 and 475–500 nm are assigned to metal-to-ligand charge-transfer (MLCT) and

Table 2
IR and electronic absorption spectral data for complexes **1**–**13**

Compound	IR spectra (cm^{-1})		Solvent	Electronic spectra λ (nm) (log ε)
	ν (C=N)	ν (C–O)		
1	1612	1527	$CHCl_3$	260, 305, 408
			DMF	269, 302, 354[a], 399
2	1615	1526	$CHCl_3$	266, 305, 357, 420[a], 450[a]
			DMF	269, 302, 355, 409[a]
3	1613	1527	$CHCl_3$	257, 305, 407, 480[a]
			DMF	272, 303, 402, 500[a]
4	1616	1528	$CHCl_3$	268, 290[a], 350,[a] 420,[a] 500[a]
			DMF	242, 298, 349,[a] 410[a]
5	1615	1527	$CHCl_3$	271, 309, 356, 420[a]
			DMF	271, 302, 354,[a] 416[a]
6	1602	1527	$CHCl_3$	263, 303, 490, 500[a]
			DMF	272, 299, 423
7	1605	1526	$CHCl_3$	261, 307, 415
			DMF	270, 303, 411
8	1611	1529	$CHCl_3$	263, 299, 415, 480[a]
			DMF	270, 298, 412
9	1615	1528	$CHCl_3$	262, 306, 350,[a] 400,[a] 480[a]
			DMF	274, 308, 354,[a] 399, 424
10	1612	1527	$CHCl_3$	260,[a] 299,[a] 335,[a] 431[a]
			DMF	269, 293,[a] 358,[a] 400[a]
			EtOH	210, 240,[a] 260, 300, 360, 420
11	1614	1528	$CHCl_3$	263, 302, 405, 480[a]
			DMF	269, 301, 401, 432, 475[a]
12	1613	1528	$CHCl_3$	270, 306, 350,[a] 400
				272, 303, 404
13	1623	1518	$CHCl_3$	270,[a] 300,[a] 320,[a] 492, 590,[a] 1008
			EtOH	252(4.6), 300,[a]380(4.2), 477(4.1), 600(3.05), 1008(2.91)

[a] Shoulder.

$^1A_{1g} \rightarrow {}^1B_{1g}$ transitions [12], respectively. Surprisingly, the electronic spectra of complex **13** in EtOH and $CHCl_3$ are quite different from those of the other complexes **1**–**12** (Table 2). The absorbance at 600 nm in the spectra of **13** probably originates from a $Pd(d\pi) \rightarrow \pi^*$ transition. The band at 1008 nm, which is not characteristic for bis(salicylaldimine) Pd^{II} helates, is similar to the near-IR region bands (800–1100 nm) recently reported for (naphthylazo)imidazole-(catecholate) Pd^{II} [13a] and some Cu^{II} complexes [13b] and assigned to the inter-ligand charge transfer process (LLCT) [13c].

The ^1H NMR spectral results obtained for some L^xH ligands and their complexes in $CDCl_3$, with their assignments, are given in Table 3. The proton resonance, appearing as a broad low intensity singlet at $\delta = 11.45$–14.86 ppm in the spectra L^xH due to the OH/NH protons involved in intramolecular H-bonding, is absent in the ^1H NMR spectra of their complexes. In contrast to expectation, all protons of azomethine and salicylic moieties of these complexes were shifted upfield from the free ligand peaks, while the aniline ring protons exhibit either downfield shift or remain unchanged (Table 3). Similar magnetic shielding effects have been previously observed in Schiff base complexes of Pd(II), Zn(II), Co(II) and Cu(II) [14].

3.2. Electrochemistry of the complexes

The CV of complexes **1**–**12** are similar to each other and are composed of an irreversible oxidation peak (Fig. 1) which is assigned to the Pd(II)-phenoxide/Pd(II)-phenoxyl couple within potentials ranging from 1.07 to 1.16 V, except for the complexes **6** and **12**. Upon reversal of scan direction, no cathodic peak was observed for all Pd complexes in our working range from +1.3 to −1.0 V. The CV of **1**, **9** and **12** were studied in MeCN versus SCE, as well. The electrochemical behavior of **1** in MeCN was different from the complexes **9** and **12**. As shown in Fig. 2, a quasi-reversible oxidation peak was observed at around +1.29 V versus SCE for (**1**)

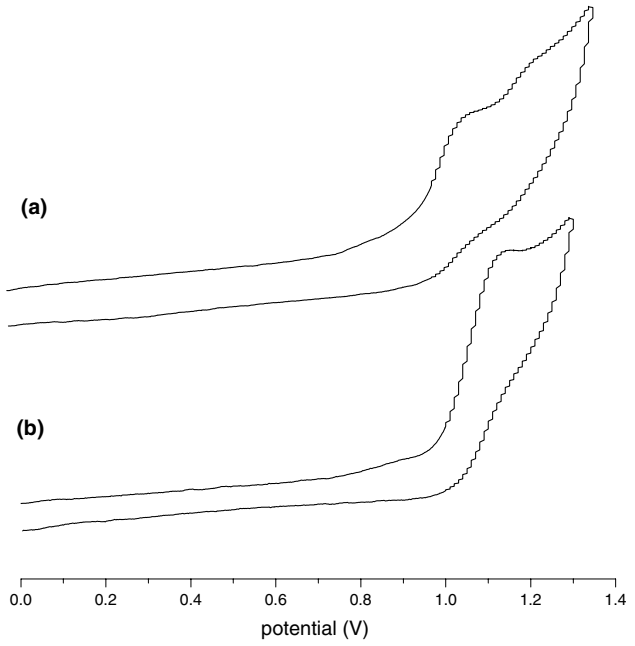

Fig. 1. (a) Cyclic voltammogram of 1.05×10^{-3} M (**3**) in DMF at room temperature vs. SCE. (b) Cyclic voltammogram of 1.24×10^{-3} M (**9**) in DMF at room temperature vs. SCE.

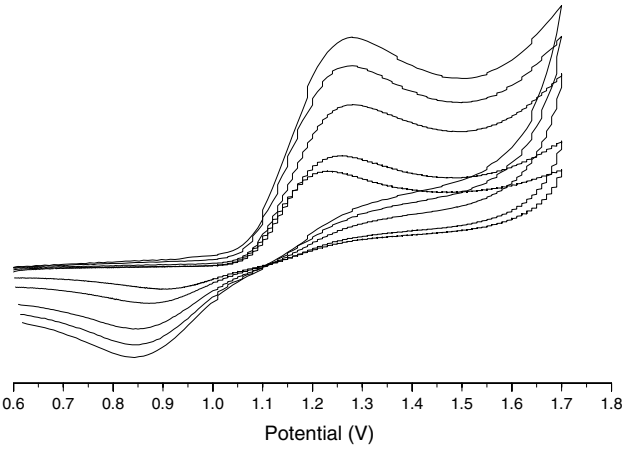

Fig. 2. Cyclic voltammogram of 9.85×10^{-4} M (**1**) in acetonitrile at room temperature vs. SCE.

Table 3
^1H NMR spectral data L^1H, L^7H, $L^{12}H$ and their Pd^{II}-complexes (δ ppm)

Compound	OH	CH=N	Sal.H	PhH	$C(CH_3)_3$
L^1H	13.65	8.63 (s, 1H)	7.21 (d, J = 2.2 Hz, 1H)	7.22–7.46 m	1.33, 1.48
(**1**)		7.89 (d, J = 9.6 Hz, 2H)	7.45 (d, J = 2.7 Hz, 1H)	7.47–7.56 m	0.82, 1.22
			6.93 (d, J = 2.7 Hz, 2H)		
			7.24 (d, J = 2.6 Hz, 2H)		
L^7H	13.49	8.60 (s, 1H)	7.22 (d, J = 2.8 Hz, 1H)	7.52 m, 7.15 m	1.33, 1.48
(**7**)		7.86 (d, J = 8.7 Hz, 2H)	7.47 (d, J = 2.3 Hz, 1H)	7.52–7.55 m	0.81, 1.21
			6.92 (d, J = 2.3 Hz, 2H)		
			7.24 (d, J = 2.5 Hz, 2H)		
L^{12}	13.86	8.64 (s, 1H)	7.22 (d, J = 2.7 Hz, 1H)	7.21–7.39 m	1.33, 1.49
(**12**)		8.0 (d, J = 7.7 Hz, 2H)	7.44 (d, J = 2.8 Hz, 1H)	7.22–7.47 m	1.22, 1.34
			6.94 (d, J = 2.4 Hz, 2H)		1.49
			7.22 (d, J = 2.4 Hz, 2H)		

in MeCN. The CV of the other Pd complexes was not studied in MeCN due to their lower solubility in MeCN compared to that in DMF. The E_{pa} values of (**1**)–(**12**), unlike E_{pa} of L^xH [8d], did not correlate with the electron-donating/withdrawing power of the aniline substituents.

The positive slope obtained in the plot of the peak current (i_p) versus the square root of the voltage scan rate ($V^{1/2}$) within the range of 100–1000 mV/s indicates diffusion controlled electron exchange reactions at the first oxidation peak potentials of all the Pd complexes [15]. A negative slope was obtained when the current function $[i_p/(CV^{1/2})]$ for the first oxidation peaks was plotted against LogV, indicating a reversible electron exchange followed by a chemical reaction [15]. Appearance of irreversible peaks in the cyclic voltammogram can be explained by a higher rate of the chemical reaction following the electrochemical one.

3.3. Chemical oxidation of the complexes

Recently we have found that in the chemical oxidation of some bis(*N*-aryl-3,5-di-Bu^t-salicylaldiminato) copper(II) complexes with the one-electron oxidant $(NH_4)_2Ce(NO_3)_6$ in acetonitrile, along with decreasing of the Cu(II) signal intensity, the generation of directly coordinated phenoxyl radical complexes are also produced [8d]. The present investigation of the oxidative behavior of complexes containing 4-CH_3, 4-F and 4-Br, reveals the formation of strong isotropic radical signals (Fig. 3(a)) with $g = 2.0114$ ($\Delta H = 22$ G), 2.0086 ($\Delta H = 10.5$ G) and 2.0076 ($\Delta H = 12.5$ G), respectively, in the presence of excess oxidant in $CHCl_3$ at 300 K. The relatively stable behaviors and the increased *g*-factors of these radicals compared to that for free 2,4-di-tert-butylphenoxyl radical ($g = 2.0045$) [16], suggest significant metal-orbital contribution to the SOMO of phenoxyl radical and the generated radical species can be assigned to directly coordinated Pd^{II}–phenoxyl radical complexes. It is interesting that under the same conditions upon oxidation of 2-CH_3 and 2-Br substituted complexes anisotropically broadened ESR spectra typical for strongly immobilized nitroxide radicals [17] with parameters $g_{\|} = 2.0061$, $g_{\perp} = 2.0072$, $A_{\|} = 37.5$ G, $A_{\perp} = 5.38$ G, $A_{iso} = 16.0.9$ G and $g_{\|} = 2.0048$, $g_{\perp} = 2.0064$, $A_{\|} = 37.5$ G, $A_{\perp} = 4.96$ G, $A_{iso} = 15.81$ G were observed (Fig. 3(c)). The appearance of such anisotropic spectra suggests that the generated nitroxide radicals are rigidly fixed in the polycrystalline matrix. Since the reaction mixture

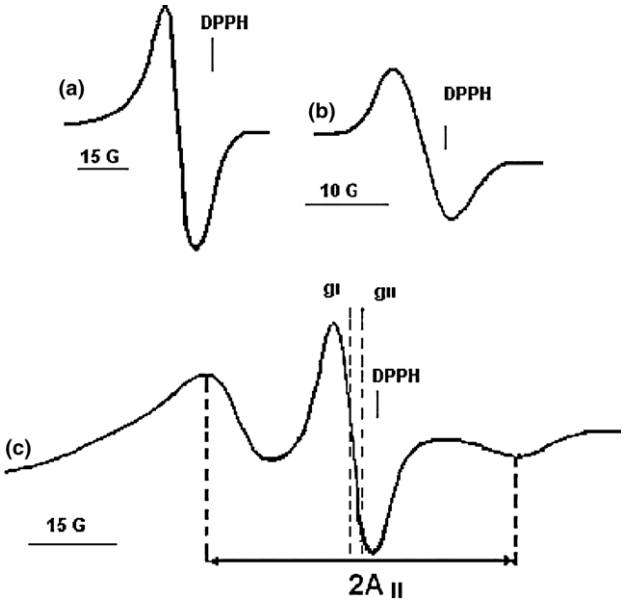

Fig. 3. ESR spectra of the oxidized compounds with $(NH_4)_2Ce(NO_3)_6$ in $CHCl_3$: (a) complex **7** at 300 K; (b) L^9H ligand at 130 K; (c) complex **9** at 300 K.

was heterogeneous due to insolubility of the oxidant in $CHCl_3$ this result is not surprising. When L^xH and the oxidant are mixed in $CHCl_3$ at 300 K and instantly cooled to 130 K, the isotropic singlet ($g = 2.0049$–2.0055) assignable to the free phenoxyl radicals generated from free ligands was observed (Fig. 3(b)).

3.4. Catalytic reduction of nitrobenzene by complexes *1*–*13*

The present investigation has shown that except for (**6**) (X = 2-Br) and (**13**) (X = 5,6-benzo), all of the complexes exhibit catalytic activity in the hydrogenation of nitrobenzene under normal pressure of H_2, 760 Torr, in DMF solution at 25 °C,. Nitrobenzene, as identified by means of IR scanning, was completely reduced to aniline. Although addition of $NaBH_4$ ($1.0–8.0 \times 10^{-5}$ mol) to the catalysts solution prior to the introduction of H_2 accelerated their catalytic activity, the hydrogenation generally did not need any preliminary activation (Table 5, Fig. 4). The conditions, initial rate absorption of H_2 and specific activity for **1**–**12**, as well as for bis(*N*-4-CH_3Ph-salicylaldiminato)Pd(II), are presented in Table 5. The course of reduction for some PdL^x_2 cata-

Table 4
Cyclic voltammetry data (VSR = 100 mV/s) for complexes **1**–**7**, **9**, **12** in DMF

Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**9**	**12**
[a]E_a (V)	1.10	1.16	1.14	1.17	1.14	1.16, 1.27	1.15	1.09	1.07, 1.25

[a] E_a represents oxidation peak potentials.

Table 5
Conditions, initial rate of H_2 absorption, catalytic activity of Pd^{II}-complexes at 1 atm. of H_2 and at 25 °C

Compound	$[C_{cat}]$ (10^{-3} mol l^{-1})	C_{PhNO2} (mol/l)	Initial rate of H_2 W Absorption (ml/min)	Specific activity Mol H_2/mol-cat (min)
(**1**) (X = H)	2.08	0.392	5.50	5.41
(**2**) (X = 2-F)	1.06	0.156	3.67	5.68
[a](**2**)	1.32	0.196	2.56	3.97
(**3**) (X = 4-F)	1.05	0.196	6.6	13.20
[a](**3**)	1.06	0.245	1.17	3.19
(**7**) (X = 4-Br)	1.27	0.157	9.9	12.8
(**9**) (X = 4-CH_3)	1.07	0.176	5.0	7.67
(4-CH_3Ph-sal)$_2$ Pd	2.02	0.176	1.13	1.09
(**12**) (X = 4-^{t}Bu)	1.06	0.157	2.75	3.36

[a] Reduction carried out in the absence of $NaBH_4$.

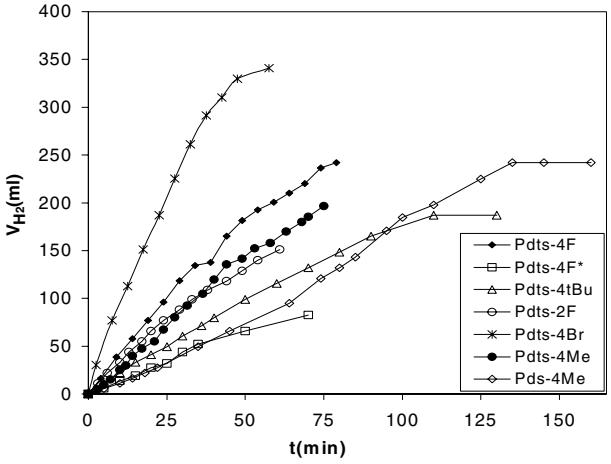

Fig. 4. Hydrogenation of $PhNO_2$ for some **1**–**12** complexes at 25 °C, in the presence of a catalytic amount of $NaBH_4$ (1×10^{-4}–8×10^{-5} mol) in DMF; (**3**) (Pdts-4F), (**3**) (Pdts-4F*) in the absence of $NaBH_4$, (**2**) (Pdts-2F), (**7**) (Pdts-4Br), (**9**) (Pdts-4Me), (**12**) (Pdts-4*t*Bu), (*N*-4-MePh-salicylaldiminato)$_2$Pd (Pds-4Me).

lysts is shown in Fig. 3. The initial rate of H_2 absorption and the specific catalytic activity for catalyst **9** are approximately four and seven times greater compared to those for its non-*t*-butylated bis(*N*-4-CH_3Ph-salicylaldiminato)Pd(II) analogs. These results indicate that introduction of Bu^t groups on the salicylaldehyde ring increases the catalytic activity of the complexes. The electron-donating Bu^t group probably increases the electron density on the Pd atom, which is subjected to electrophilic attack by a nitro group of $PhNO_2$. While the steric hindrance of *o*-substituents reduces the hydrogenation rate, there is less correlation between initial absorption rate of H_2 and electron-donating/withdrawing effect of the *p*-substituents on the aniline fragment. The specific catalytic activity of the Pd complexes decreases in the order 4-F > 4-Br > 4-CH_3 > H > *t*-Bu (Table 5). This trend was not consistent with the electron-releasing/withdrawing effect of the substituents. It is thought that the orthogonality of the anilinic and salicylideneimine planes might cause the lower sensitivity of the absorption rate of H_2 to the electronic factors on the aniline ring substituents.

In conclusion, the prepared bis(*N*-aryl-3, 5-Bu^t_2-salicylaldimine)palladium(II) complexes exhibit interesting spectral, electron-transfer and catalytic behaviors. The introduction of the two *t*-Bu groups on the salicylic ring increases the catalytic activity and oxidative reactivity of the Pd^{II}–salicylaldinine complexes in the hydrogenation of $PhNO_2$. The chemical oxidation of the title complexes with cerium(IV) nitrate, besides directly coordinated Pd(II)-phenoxyl radical complexes, also generates nitroxide radicals.

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