Oxovanadium(IV), Nickel(II) and Palladium(II) Complexes of Tridentate Salicylaldiminates Derived from 2,4-Di-tert-butyl-6-aminophenol

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Tridentate Salicylaldiminates, ESR, Catalytic Activity

Several new binuclear nickel(II), oxovanadium(IV) and palladium(II) complexes (ML\textsuperscript{2}) of tridentate salicylaldimines (L\textsuperscript{X}H\textsubscript{2}) obtained from substituted salicylaldehydes and 2,4-di-tert-butyl-6-aminophenol, as well as mononuclear nickel(II) and oxovanadium(IV), MQ\textsuperscript{X}-nH\textsubscript{2}O, complexes with hydrogenated L\textsuperscript{X}H\textsubscript{2} ligands (Q\textsuperscript{X}H\textsubscript{2}) have been prepared and their spectroscopic, magnetic and catalytic activity (for PdL\textsuperscript{2}) have been investigated. NiL\textsuperscript{2} and VOQ\textsuperscript{X} complexes when dissolved in pyridine, take up three or two pyridine molecules to form six coordinated complexes, respectively. The Ni(II) and VO(IV) complexes obtained from Q\textsuperscript{X}H\textsubscript{2} can be formulated as NiOQ\textsuperscript{X}-3H\textsubscript{2}O and VOQ\textsuperscript{X}H\textsubscript{2}O. All VO(IV) complexes have been characterized by ESR parameters. It has been found that some PdL\textsuperscript{2} complexes without any preliminary activation, in EtOH, THF and DMF exhibit high catalytic activity in the hydrogenation of nitrobenzene or cyclohexene at room temperature and at 30 - 40 °C under 760 torr H\textsubscript{2}. When this reaction has been carried out in the ESR cavity at room temperature the triplet of 12 line multiplets due to the nitroxyl type coordinated radical (g = 2.013, A\textsuperscript{N} = 10 G, A\textsuperscript{H} = 0.8 G) was detected.

Introduction

In recent years there has been considerable interest in the chemistry of transition metal complexes of tridentate dibasic salicylaldimines [1 - 3]. These ligands force the metal ions into close proximity leading to metal complexes with unusual magnetic and structural properties. Particular interest has been focused towards the magnetic coupling phenomena and the catalytic activities in biological model dinuclear complexes [4]. The palladium complexes were found to be effective catalysts for promoting specific carbon-carbon, carbon-oxygen, carbon-nitrogen and nitrogen-hydrogen bond formation under mild conditions [7].

The coordination chemistry of some transition metals with potentially redox-active chelating ligands such as bi-, tri- and tetradeinate salicylaldiminates, napthaldiminates, azo ligands, \(\beta\)-ketoamines and other ligands containing sterically hindered phenol fragments have been studied by us [8 - 10]. In these studies complexes along with unexpected structures, coordinated radical ligand intermediates, as well as high redox-reactivity of Cu(II) and Pd(II) salicylaldiminates towards PbO\textsubscript{2} and triarylporphinines have been found.

Scheme 1.

The present work is part of a research plan to study the syntheses of transition metal complexes with redox-active ligands containing sterically hindered phenol groups and their structure, spectroscopic behavior, redox-reactivity, and catalytic activity in various reactions. We prepared and characterized a series of binuclear metal complexes, ML\textsuperscript{X}
Table 1. Analytical data for the QX⁻ligands and the MLX² and MQX⁻nH₂O complexes.

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<th>Compound</th>
<th>Yield</th>
<th>M.p. °C</th>
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<th>Elemental analyses, Found/Calcd [%]</th>
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<th>H</th>
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<td>VOQ¹-H₂O</td>
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(M = VO, Ni, Pd), where Lₓ represents the dianions of tridentate N-(3,5-di-tert-buty1-2-hydroxyphenyl) salicylaldimines, (formed by the condensation of substituted salicylaldehydes and 2,4-di-tert-butyl-6-aminophenol) and their hydrogenated MQₓ⁻ₙH₂O analogues, with Qₓ⁻H₂ obtained by the hydrogenation of the appropriate LₓH using NaBH₄ as presented in Scheme 1. Binuclear CuLₓ complexes have previously been reported [9b], while our attempts to prepare the similar binuclear complexes of Co(II) with LₓH₂ ligands were not successful.

**Experimental**

The IR spectra were obtained on a Carl Zeiss Jena Specord M 80 spectrophotometer in the range of 4000 - 400 cm⁻¹ on KBr discs. Electronic spectra were recorded on a Carl Zeiss Jena Specord M 40 spectrophotometer in the range of 200 - 900 nm. Magnetic susceptibilities were measured by the Faraday technique, from liquid nitrogen temperature to room temperature, and diamagnetic corrections were made using Pascal's constants. The apparatus was calibrated by the use of Hg[Co(NCS)₄]. X-Band ESR spectra were recorded in solid state and in solution at 300 and 77 K on a Radiopan model SE/X-2547 X-Band spectrometer. DPPH (g = 2.0036) was used as an external standard. The ESR parameters of the complexes were determined directly from the spectra. The magnetic field was calibrated using a standard Mn²⁺ sample. Reported values involve errors within ±0.002 for g-values and ±0.05 G for A-values of VOL. The errors for g-factor and hyperfine splitting constants (hfsc) (A⁻¹ and A¹) are ±0.0005 and ±0.005 G, respectively.

**Preparation of the compounds**

Salicylaldehyde, all solvents and metal acetates were commercial products (Merck) and used without further purification. N-(3,5-di-tert-butyl-2-hydroxyphenyl)-salicylaldimine (LₓH₂) and MLₓ (M = Ni(II), VO(IV), Pd(II)) compounds were synthesized as previously described [9, 11(a), (b)] by mixing equivalent amounts of ligands and metal acetates in a 1:1 ligand to metal molar ratio. The substituted salicylaldehydes were prepared according to the literature [11(c)], using commercially available reagents.

For comparative purposes, the nickel(II) and oxovanadium(IV) complexes (MQₓ⁻ₙH₂O) with hydrogenated LₓH (abbreviated as QₓH) were prepared according to [10(c)].

N-(3,5-di-tert-butyl-2-hydroxyphenyl)-2'-hydroxyphenylbenzylamines (QₓH) were prepared from LₓH (x = 1, 2, 3) by the following procedure. NaBH₄ (0.05 mol)
was added slowly (small portions of about 10 - 15 mg) to 0.01 mol stirred solutions of L¹H in 40 - 50 ml of isopropanol for 15 - 20 min. Stirring was continued for another 30 - 40 min and the cooled mixture was then poured into 150 - 200 ml water. After cooling to room temperature the solution was stirred for 1 h and allowed to stand for 3 - 4 h. The precipitated white crystals were collected by filtration and then washed with water, dried under vacuum and recrystallized from a hexane-acetone mixture, yield 85 - 95%. Analysis for Q'H: M. p. 113 °C. - UV/vis (C₂H₅OH): Am max = 210, 240, 280, 450 nm. - IR (pellet): ν = 3345 cm⁻¹ (N-H, O-H). - *H NMR (200 MHz, CDCl₃): δ = 1.31 (s, 9 H, C(CH₃)₃), 1.43 (s, 9 H, C(CH₃)₂), 3.35 (s, 2 H, CH₂), 4.38 (s, 1 H OH), 6.72, 6.93, 7.03, 7.28 (4 x d, J = 2.4 Hz, 4 H, Ar-H), 6.75, 6.85 (2 x t, J = 12.1 Hz, 2 H, Ar-H), very broad centered at 8.5. - C₂H₅NO₂, calcld. C 77.01, H 8.93, N 4.28; found C 77.14, H 8.66, N 4.22.

The m. p's of all complexes exceed 250 °C. Elemental analyses, melting points and yields are given in Table 1.

Hydrogenation of nitrobenzene was carried out in a thermostatic glass vessel (25 cm³) at 30 - 40 °C under 760 torr H₂ and with vigorous stirring in EtOH, THF and / or DMF. Nitrobenzene (1 - 4 x 10⁻⁴ mol) in 15 ml solvent was transferred into a vessel, while 2 - 6 x 10⁻⁵ mol PdL¹ was added through the side bend. Then the reaction mixture was deoxygenated and hydrogen gas was pumped into the vessel. After stirring for 15 - 20 min, an excess of H₂ was added and the volume of absorbed H₂ was measured periodically.

Results and Discussion

The analytical data of the ML¹ complexes indicate 1:1 metal-ligand ratio stoichiometry, and hence the ligands (L¹H₂) act as tridentate dibasic ligands (Table 1). As confirmed by the ESR examination the samples of ML¹ and MQ¹ nH₂O except the Co(II) compounds did not exhibit evidence for the formation of radical species during complexation.

The stretching vibrations ν(CH=N) in the IR spectra of ML¹ were detected in the 1604 - 1612 cm⁻¹ region and shifted to lower frequencies relative to free L¹H₂ (1620 - 1630 cm⁻¹) indicating that coordination has taken place through
the azomethine nitrogen atom of the ligands. The stretching frequency of the phenolic OH of L\(^3\)H\(_2\) appeared at 3520 - 3530 cm\(^{-1}\) and disappeared in the IR spectra of ML\(^x\) and MQ\(^x\) (Table 2). The \(\nu\)(V=O) bands of the VOL\(^x\) complexes occur at 910 - 960 cm\(^{-1}\) which is in the usual range (960±50 cm\(^{-1}\)) observed for the majority of VO(IV) complexes [13]. New bands, which are absent in the spectra of all the free ligands, were observed in the 600 - 400 cm\(^{-1}\) region, and were assigned to \(\nu\)(M-O) and \(\nu\)(M-N) (Table 2) [14].

In the IR spectra of MQ\(^x\)n(H\(_2\)O) compounds obtained from hydrogenated tridentate benzylamines, the \(\nu\)(OH) and \(\nu\)(NH) stretching modes appear as overlapping broad absorptions centered in the 3238 - 3250 cm\(^{-1}\) range.

**Complexes of Ni(II)**

The NiL\(^1\) complex is diamagnetic in agreement with a square planar geometry for the metal atom in the dimer. However, the 5-substituted NiL\(^2\) and NiL\(^3\) complexes show magnetic moments in the 3.06 - 3.42 B.M. range, which supports octahedral structures [15]. Note that the magnetic moments of these compounds remain essentially unchanged over the temperature range 80 - 300 K. It is known that in O\(_6\) symmetry Ni(II) complexes have a low orbital contribution (\(\mu_{\text{eff}} = 2.83 - 3.4\) B.M.), while those having a T\(_d\) symmetry are subject to a much higher orbital contribution (\(\mu_{\text{eff}} = 3.5 - 4.2\) B.M.), due to the presence of orbitally degenerate ground states [13]. Consequently, considering the small orbital contribution to the effective magnetic moments and the temperature independent behavior of \(\mu_{\text{eff}}\), we suggest a pseudo-octahedral structure for the metal environment in the solid state. This configuration can be reached by axial Ni-O-Ni bridges of planar dimer moieties.

The electronic spectra of the NiL\(^x\) complexes reveal very similar spectral patterns in THF or EtOH solution with a single ligand field band at 480 for NiL\(^1\) and NiL\(^2\), and at 560 nm for NiL\(^3\) characteristic of diamagnetic square-planar Ni(II) complexes (Table 2). These bands may be assigned to \(^1A_{1g}\) \(\rightarrow\) \(^1A_{2g}\) and \(^1A_{1g}\) \(\rightarrow\) \(^1B_{1g}\) transitions [12], respectively. Three new d-d bands appear in the 500 - 900 nm range with molar extinction coefficient in the range 6 - 10 M\(^{-1}\)cm\(^{-1}\) generated on dissolving of NiL\(^x\) in pyridine (Table 2) probably caused by NiL\(^x\)-3Py adduct type octahedral complexes. The bands observed in the regions of 440 - 470, 550 - 560 and 860 - 875 nm in pyridine are assigned to spin-allowed transitions \(^3A_{2g}(F)\) \(\rightarrow\) \(^3T_{2g}(P)\), \(^3A_{2g}(F)\) \(\rightarrow\) \(^3T_{1g}(F)\) and \(^3A_{2g}\) \(\rightarrow\) \(^3T_{2g}(F)\), respectively, for octahedral Ni(II) complexes [12, 15].

It is of interest to compare the complexability ability of tridentate L\(^3\)H\(_2\) with their hydrogenated potentially tridentate Q\(^3\)H\(_2\) analogs (Scheme 1). The analytical and spectral data of Q\(^3\)H\(_2\) and their Ni(II) chelates (NiQ\(^3\)-3H\(_2\)O) are presented in Tables 1 and 2. The results of elemental analyses and the IR and electronic spectral data of Ni(II) complexes with Q\(^3\)H\(_2\) indicate to the formation of monomeric octahedral NiQ\(^3\)-3H\(_2\)O complexes. The room temperature magnetic moments and electronic spectra in chloroform are typical for octahedral Ni(II) complexes and differ from those of NiL\(^x\) in CHCl\(_3\) and EtOH. These complexes exhibit three low intensity bands in the 375 - 870 nm range which are attributed to d-d transitions in octahedral field.

**Complexes of VO(IV)**

The oxovanadium(IV) complexes belong to the S = 1/2 system and it is expected that the magnetic moments of the magnetically dilute complexes would be very close to the spin-only magnetic moment, as the spin-orbit coupling constant is positive and the orbital contribution is almost completely quenched [13]. The room temperature magnetic moments of VOL\(^x\) (1.57 - 1.63 B.M.) are slightly lower than the expected spin-only moment 1.73 B.M for the d\(^1\) system [13], showing a weak antiferromagnetic exchange interaction between the neighboring VO(IV) ions. The magnetic moments of the complexes remained practically unchanged in the range 80 - 300 K and obey the Curie-Weiss law with Weiss constants \(\theta\) in the range of -1.2 to -0.9 K.

Interestingly the \(\mu_{\text{eff}}\) values of these complexes as estimated from ESR spectra by using the equation: \(\mu_{\text{eff}} = 1/2 \left( g^2 + 2g^2_1 \right)^{1/2} \) [16] are in the range of 1.71 - 1.74 B.M. They agree well with spin-only values expected for magnetically diluted VO(IV) complexes.

The electronic spectra of VOL\(^x\) complexes in chloroform (Table 2) exhibit three absorption bands at 828 - 848 (I), 625 - 632 (II), and 510 - 516 (III) nm, which are assigned to the \(d_{xy} \rightarrow d_{x^2 - y^2}\), \(d_{xy} \rightarrow d_{z^2 - y^2}\), \(d_{xy} \rightarrow d_z\) transitions, respectively,
| Compound | Solvent | $g_{iso}$ | $g_{||}$ | $g_{\perp}$ | $A_{iso}$ | $A_{||}$ | $A_{\perp}$ |
|----------|---------|----------|--------|--------|---------|--------|---------|
| VOL\textsuperscript{1} | Toluene | 1.998   | 1.941  | 2.027  | 99.4   | 182.2  | 57.9    |
|         | CHCl\textsubscript{3} | 1.985   | 1.957  | 1.999  | 75.2   | 135.1  | 45.2    |
| VOL\textsuperscript{2} | Toluene | 1.996   | 1.985  | 2.002  | 88.4   | 172.6  | 46.3    |
| VOL\textsuperscript{3} | Toluene | 1.987   | 1.956  | 2.003  | 79.2   | 121.5  | 58.1    |
| VOL\textsuperscript{5} | Toluene | 2.003   | 1.948  | 2.031  | 99.6   | 185.2  | 56.8    |
| VOQ\textsuperscript{1},H\textsubscript{2}O | CHCl\textsubscript{3} | 1.959   | 1.942  | 1.967  | 105.7  | 187.7  | 64.7    |
| VOQ\textsuperscript{2},H\textsubscript{2}O | CHCl\textsubscript{3} | 1.978   | 1.964  | 1.985  | 104.8  | 190.3  | 57.1    |
| VOQ\textsuperscript{3},H\textsubscript{2}O | CHCl\textsubscript{3} | 1.995   | 1.975  | 1.975  | 105.1  | 191.2  | 62.1    |

Table 3. ESR parameters of the VOL\textsuperscript{x} and VOQ\textsuperscript{x},H\textsubscript{2}O complexes.

According to the Ballhausen–Gray energy level scheme [17]. Note that although this sequence of energy levels was proposed by Ballhausen and Gray in 1962, the same sequence of energy levels for VO(IV) complexes was referenced by A.Syamal and co-workers, in all of their paper, to Vanquick-\textsuperscript{enbome} and McGlynn [18]. A comparison of the spectra recorded in pyridine with those obtained in toluene indicates that upon going from non-coordinating toluene to strongly coordinating pyridine, the band I shifts to lower energy and band III to higher energy. A minor blue shift was detected also in the positions of band II upon going from toluene to pyridine (Table 2). Thus, our investigation indicates that the $^2B_2 (d_{xy}) \rightarrow ^2E(d_{xz}, d_{yz})$ (I) and $^2B_2(d_{xy}) \rightarrow ^2A_1 (d_{z^2})$ (III) transitions shift to lower and higher energies, respectively, upon going from non-coordinating toluene to coordinating pyridine solvent. This fact seems to indicate that the oxovanadium(IV) complexes, when dissolved in pyridine, combine with two molecules of pyridine to form six-coordinated adducts. The electronic spectral changes on adduct formation of VOL\textsuperscript{x} with pyridine can be interpreted according to the Ballhausen-Gray scheme. The axial and equatorial coordination of pyridine molecules leads to the decrease of $E_{xy} \rightarrow E_{xz,yz}$ and increase $E_{xy} \rightarrow E_{z^2}$ energy separations, respectively. Since the energy of the $E_{xy} \rightarrow E_{xz,yz}$ transition decreases, the increased axial $\pi$-bonding will stabilize the $d_{xz,yz}$ pair more than the in-plane $\pi$-bonding of $d_{xy}$.

The ESR spectrum of VOL\textsuperscript{1} in polycrystalline state exhibits a single broad line at $g_{av} = 1.99$ (300 K) and a low intensity resonance at $g = 4.1$ (77 K) due to the $\Delta M_S = \pm 2$ transition. For other VOL\textsuperscript{x} compounds at 77 K along with a weak signal at $g = 4.32$, complicated signal consisting of 10–12 broad lines at ca. $g = 2.0$ was observed. The room-temperature isotropic ESR spectra of VOL\textsuperscript{x} in chloroform and toluene consist of the usual eight hyperfine lines resulting from coupling of the unpaired electron to the
$^{51}\text{V}$ (I = 7/2) nucleus. However, the frozen-solution spectra of these complexes in CHCl$_3$ were quite different from the corresponding spectra in toluene (Fig. 1). For example, in the spectrum of VOL$^1$ in CHCl$_3$ at 77 K, the $g_{||}$ components appeared with a well-resolved hyperfine structure ($A_{||} = 135$ G), but the $g_{\perp}$ components were not resolved. The spectrum of the same complex in toluene shows well resolved $g_{\perp}$ components, but along with some other hyperfine lines the broadening and splitting of high field $g_{||}$ components were also observed (Figs. 1a, b). Similar features were observed for VOL$^3$ and VOL$^5$. Such behavior of the spectra may be caused by structures having almost identical ESR parameters or from anisotropic g and hyperfine tensors [18, 19]. Some low intensity satellite lines appeared in the frozen solution spectra, probably indicate the presence of a dimeric structure [20]. Although the ESR spectra of VOL$^5$ in toluene and CHCl$_3$ are typical for monomeric VO(IV) and all $g_{||}$ and $g_{\perp}$ components are well resolved (Fig. 1c), the value of $A_{\perp}$ calculated from formula $(3A_{iso} - A_{||})/2$ was in disagreement with that determined directly from the experimental spectrum. Analysis of the ESR spectra of VOL$^x$ complexes showed that in toluene they have $g_{\perp}$ values of ca. 2 and $g_{||} < 2$ with $A_x > A_y = A_z$, and $g_x < g_y < g_z < 2$ with $A_x > A_y = A_z$ in CHCl$_3$, which typical for axial symmetry [21]. There was no splitting observed of the $x$ and $y$ features.

It is interesting to compare the VOL$^x$ complexes with corresponding compounds obtained from hydrogenated L$^x$H$_2$, abbreviated as Q$^x$H$_2$ and VOQ$^x$.H$_2$.O. As can be seen from Tables 2 and 3 the electronic spectral data and ESR parameters of VOQ$^1$.H$_2$.O are different from those for VOL$^x$ complexes. The magnetic and spectral behavior of VOQ$^1$.H$_2$.O are typical for mononuclear VO(IV) compounds. In the latter complexes the values of the g-factors are reduced and the values of the d-d transition energy are increased. This effect is probably caused by the stronger ligand fields of Q$^x$H$_2$ ligands compared to their salicylaldimine L$^x$H$_2$ analogs.

**Complexes of Pd(II)**

In the electronic spectra of the PdL$^x$ compounds in THF or ethanol solutions low intensity bands at 410 – 145, 435 – 450 nm, attributable to the transitions $^1A_{1g} \rightarrow ^1B_{1g}$ and $^1A_{1g} \rightarrow ^1A_{2g}$ [12], respectively, were observed. The intense band observed in the UV region at 310 – 335 nm has undoubtedly charge transfer nature. In the electronic spectra of PdL$^3$ in pyridine, only PdL$^1$ and PdL$^4$ complexes show a new single absorption maximum at 673 nm with molar extinction coefficients of $10^4$ and $10^2$ M$^{-1}$cm$^{-1}$, respectively. These two complexes exhibit high catalytic activity in the hydrogenation of nitrobenzene.

**Nitrobenzene hydrogenation catalyzed by complexes PdL$^x$**

Palladium-mediated catalysis in organic synthesis has received much attention [7, 22]. It is known that some Pd(II) complexes (Pd-salen, Pd-azo complexes, Pd-nitroso complexes and Pd-alizarin) show catalytic activity in the hydrogenation of aromatic nitro compounds and of olefins [23, 24]. Our investigation has shown that among the PdL$^x$ complexes...
Table 4. Hydrogenation of nitrobenzene in the presence of PdL\textsuperscript{x} complexes under 760 torr H\textsubscript{2} in various solvents.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Temp. °C</th>
<th>Solvent</th>
<th>C\textsubscript{cat} \textsuperscript{*} [10\textsuperscript{-7} mol/L]</th>
<th>CPhNO\textsubscript{2} [10\textsuperscript{-4} mol/L]</th>
<th>Specific activity Mol H\textsubscript{2}/mol M-min</th>
<th>Absorption rate W [ml H\textsubscript{2}/min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdL\textsuperscript{1}</td>
<td>30</td>
<td>C\textsubscript{2}H\textsubscript{3}OH</td>
<td>3.61</td>
<td>1.26</td>
<td>6.81</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>C\textsubscript{2}H\textsubscript{3}OH</td>
<td>5.82</td>
<td>1.16</td>
<td>8.89</td>
<td>1.16</td>
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<tr>
<td></td>
<td>30</td>
<td>DMF</td>
<td>2.85</td>
<td>1.26</td>
<td>0.22</td>
<td>0.0142</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>DMF</td>
<td>3.9</td>
<td>1.33</td>
<td>0.16</td>
<td>0.0125</td>
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<tr>
<td></td>
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<td>1.17</td>
<td>2.64</td>
<td>0.22</td>
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<tr>
<td></td>
<td>40</td>
<td>THF</td>
<td>3.58</td>
<td>1.28</td>
<td>3.99</td>
<td>0.32</td>
</tr>
<tr>
<td>PdL\textsuperscript{2}</td>
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<td>1.44</td>
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<td>-</td>
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<td>1.71</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>DMF</td>
<td>2.62</td>
<td>1.32</td>
<td>1.7</td>
<td>0.01</td>
</tr>
<tr>
<td>PdL\textsuperscript{4}</td>
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<td>C\textsubscript{2}H\textsubscript{3}OH</td>
<td>2.65</td>
<td>1.66</td>
<td>4.21</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>C\textsubscript{2}H\textsubscript{3}OH</td>
<td>4.42</td>
<td>0.95</td>
<td>1.52</td>
<td>0.15</td>
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<tr>
<td></td>
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<td>1.42</td>
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<tr>
<td></td>
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<tr>
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<tr>
<td></td>
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<td>4.52</td>
<td>1.77</td>
<td>1.14</td>
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\* C\textsubscript{cat}: concentration of catalyst PdL\textsubscript{x}.

Only PdL\textsuperscript{1}, PdL\textsuperscript{4} and PdL\textsuperscript{5} complexes, without any preliminary activation with NaBH\textsubscript{4} or NaOH, exhibit catalytic activity in the hydrogenation of nitrobenzene under H\textsubscript{2} pressure, 760 torr, in polar solvents such as EtOH, THF and DMF at 30 and 40 °C. This reaction also takes place at room temperature. The data of the absorption of H\textsubscript{2} with various concentrations of catalysts are presented in Table 4. The highest catalytic activity has been observed for PdL\textsuperscript{1} and PdL\textsuperscript{4} in DMF (Table 1). Note that hydrogenation of PhNO\textsubscript{2} under the above conditions using Pd(II) chelates obtained from bi- and tridentate salicylaldimines without tert-butyl groups, were unsuccessful.

In order to identify the nature of any paramagnetic intermediates formed in the process of hydrogenation, the interaction of PdL\textsuperscript{1} with PhNO\textsubscript{2} was carried out in the presence and absence of H\textsubscript{2} in THF and examined by means of ESR and electronic spectroscopy. The PdL\textsuperscript{1} complex is stable under H\textsubscript{2} atmosphere in the absence of PhNO\textsubscript{2} and this mixture does not show any radical species during 3 h at room temperature. With the PdL\textsuperscript{2} complex, which does not possesses catalytic activity in THF under the above-mentioned conditions, on mixing with PhNO\textsubscript{2} no color changes and radical intermediates were observed. By mixing solutions of PdL\textsuperscript{1} and PhNO\textsubscript{2} in the absence of H\textsubscript{2} under vacuum, the yellow solution of complex immediately turned dark green, and in the electronic spectrum of this mixture a new band at 600 nm appeared. This band probably is caused by the coordination of nitrobenzene to the Pd(II) ion. The ESR spectrum of this mixture shows a weak and poorly resolved signal at g = 2.0185, which can be assigned to a coordinated phenoxyl type radical. This signal disappears under vacuum within 2 - 3 min. When H\textsubscript{2} was introduced into this reaction mixture, a strong triplet pattern due to coupling to the \textsuperscript{14}N (I = 1) nucleus with a spacing of A\textsubscript{iso}\textsuperscript{N} = 10.66 G at g = 2.0125 was observed. There is additional, well-resolved hyperfine splitting (A = 0.8 G) for each component of the triplet consisting of 12 lines (Fig. 2a). This is most likely due to the interaction of the unpaired electron with ring protons of the coordinated PhNOH(O\textsuperscript{−}) radical. The increased value of the g-factor compared to free radicals (g = 2.003 - 2.008), undoubtedly indicates that there is a noticeable contribution from the metal d-orbitals to the molecular orbital containing the unpaired electron. The frozen glass spectrum of this mixture at 77 K exhibited an anisotropic spectrum typical for Pd(I), with parameters g\textsubscript{∥} = 2.0436, g\textsubscript{⊥} = 2.0269, A\textsubscript{∥} = 57.2, A\textsubscript{⊥} = 35.2 G due to hyperfine coupling with \textsuperscript{105}Pd (I = 5/2, natural abundance 22.2%) [25], (Fig. 2b). The increased values of the g-factors and the appearance of hyperfine splitting from \textsuperscript{14}N, \textsuperscript{1}H, and \textsuperscript{105}Pd nuclei indicate that the unpaired electron spin density is localized on the PhNOH(O\textsuperscript{−}) fragment as well as at the Pd(I) center.
Some bis[N-(2,6-di-tert-butyl-l-hydroxyphenylsalicylaldiminato)palladium(II)] complexes unlike their unhindered salicylaldiminate analogs also exhibit catalytic activity in the hydrogenation of PhNO₂ and cyclohexene under the above-mentioned conditions [26].