Stabilization and Activation of Pd Nanoparticles for Efficient CO₂-Reduction: Importance of their Generation within Supramolecular Network of Tridentate Schiff-Base Ligands with N,N Coordination Sites

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 PII:
 S0013-4686(21)00840-9

 DOI:
 https://doi.org/10.1016/j.electacta.2021.138550

 Reference:
 EA 138550

To appear in: Electrochimica Acta

Received date:8 February 2021Revised date:16 April 2021Accepted date:1 May 2021

Please cite this article as: Anna Wadas, Adam Gorczynski, Iwona A. Rutkowska, Ewelina Seta, Ewelina Szaniawska, Maciej Kubicki, Adam Lewera, Maciej Gorzkowski, Aneta Januszewska, Rafal Jurczakowski, Barbara Palys, Violetta Patroniak, Pawel J. Kulesza, Stabilization and Activation of Pd Nanoparticles for Efficient CO₂-Reduction: Importance of their Generation within Supramolecular Network of Tridentate Schiff-Base Ligands with N,N Coordination Sites, *Electrochimica Acta* (2021), doi: https://doi.org/10.1016/j.electacta.2021.138550

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Highlights

- Pd^0 is generated upon electroreduction of Pd^{II} ions in the supramolecular complex
- Pd⁰ catalytic centers are stabilized and activated by ligand N,N coordination sites
- Thus generated Pd nanoparticles exhibit high activity during CO₂-electroreduction
- CO and H₂ are the main reduction products in CO₂-saturated aqueous KHCO₃

Journal

Stabilization and Activation of Pd Nanoparticles for Efficient CO₂-

Reduction: Importance of their Generation within Supramolecular

Network of Tridentate Schiff-Base Ligands with N,N Coordination Sites

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Abstract

Tridentate Schiff base ligand L (L = $C_{14}H_{12}N_2O_3$) reacts with palladium(II) chloride, to give a complex of formula [Pd($C_{14}H_{12}N_2O_3$)Cl₂]₂·MeOH. The spectroscopic, microanalytical and X-ray crystallographic data are consistent with the view that palladium(II) ion is coordinated by two nitrogen donor atoms, with typical Pd^{II}-N distances and two chloride ligands, representing thus N,N instead of possible N,N,O coordination mode. The reduced Pd⁰ catalytic sites are electrochemically generated (by voltammetric potential cycling) within the film of supramolecular network of tridentate Schiff base ligands. The IR and XPS data of the electroreduced material are consistent with the existence of interactions between the palladium catalytic centers and the network of supramolecular ligands with N,N coordination sites. In comparison to conventional Pd nanoparticles, the CO₂-reduction current densities, which have been recorded in near-neutral KHCO₃ both under voltammetric and chronoamperometric conditions and normalized against electrochemically active surface area of palladium catalyst, are significantly higher at the supramolecular-ligand-supported Pd nanoparticles.

Key-words: palladium(II) supramolecular complex, tridentate-Schiff-base-ligand, palladium(0) catalytic centers, carbon dioxide reduction, metal support interactions

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1. Introduction

The continuously rising levels and accumulation of emitted carbon dioxide have led to severe environmental problems and concerns over climate change and possibility of global warming [1]. Low-temperature electrochemical (electrocatalytic) promotion to reduction of carbon dioxide is a promising approach to convert CO_2 and H_2O to useful chemical feedstocks that include syngas (CO + H₂), an intermediate for further Fischer–Tropsch processes, carbon-based simple organic fuels, or utility chemicals [2-14]. But the CO_2 reduction reactions (CO₂RRs) are multi-electron and multi-proton processes with considerable kinetic barriers (overpotentials) requiring development of the carefully designed electrocatalytic materials. In comparison to electrochemical water splitting and hydrogen production by electrolysis, feasibility of the efficient electrolytic CO_2 -conversion is far away from being practical [10].

The first step in CO₂RR involves electrocatalytic activation of the CO₂ molecule to form CO₂⁻⁻ radical which is believed to be energetically demanding (-1.9 V vs. standard hydrogen electrode, SHE) due to high stability of the CO₂ structure itself [2-8]. A rational model takes into account strong adsorptive (chemical) interactions of carbon dioxide with the catalytic surface thus stabilizing the CO₂⁻⁻ radical, or the reaction intermediate, and shifting the CO₂-electroreduction potential toward less negative values [4,7,10]. Copper-based catalysts have attracted special attention due to their unique properties permitting CO₂RR to oxo-hydro-carbons (e.g., alcohols, aldehydes) and hydrocarbons with substantial Faradaic efficiencies [3,4,7,15-20]. Because the CO₂RR products mentioned above are in the state of further reduced in comparison to carbon monoxide or formate, the actual electroreductions are expected to involve more than two electrons per CO₂ molecule. On the whole, by choosing an appropriate catalyst, or by proper designing its surface structure (morphology, lattice strain,

composition or intentional modification) [2,4,8], the two-electron CO_2RR to carbon monoxide or formic acid becomes feasible even at low overpotentials.

Palladium-based electrocatalysts exhibit capability to convert selectively CO_2 to CO or formate [21-30], thus permitting clean production of syngas or electrosynthesis of formic acid which of importance to preparation of fine chemicals, including pharmaceuticals, and to application in direct formic acid fuel cells. The performance of Pd catalysts is highly dependent on interfacial phenomena and the nature of binding of CO_2 to Pd surfaces, namely on the formation of intermediates such as *CO and *COOH [22,26]. Among important issues is the structure of Pd active sites which reflects its size, morphology, grain boundary, composition or even the presence of active ligands. Furthermore, distinctive interactions of carbon dioxide with palladium affecting both absorbing and adsorbing of hydrogen are known to influence both activity and selectivity of CO_2RR with respect to hydrogen evolution.

Like platinum, palladium can be considered as one of the most important metals in catalysis, also for electrochemical reactions, including oxygen reduction, formic acid oxidation, etc. [31-35]. In a case of the oxidation of HCOOH, Pd shows an excellent performance, even superior, in comparison to Pt. Despite the ability of palladium to both adsorb and absorb hydrogen readily, the chemical interactions between CO_2 and the adsorbed monoatomic H are rather weak, at least in comparison to those exiting on platinum surfaces. Indeed, surface concentration of the CO_2 -reduction products appearing in the hydrogen (*UPD-H*) region on Pd is more than 50 times lower than that on Pt [36,37]. Also, no electrolyte-soluble products of the interaction of CO_2 with the Pd-electrode surface are formed in the *UPD-H* potential range. Obviously, the nature and effectiveness of adsorptive interactions between CO_2 and the catalytic metal surface play affects the CO_2RR pathways. For example, the interfacial reduction of CO_2 to CO on platinum inhibits further CO_2 -reduction in favor of the water reduction and generation of hydrogen [38]. Because the

adsorption affinity of the surface "reduced-CO₂" is weaker on palladium, in comparison to platinum (or even other group VIIIB metals including Fe and Ni), the self-poisoning of Pd surfaces becomes less pronounced and the CO-type reduced species tend to act as the reaction intermediates [39,40]. Furthermore, the formation of substantial amounts of the bulk absorbed hydrogen on Pd affects the adsorption affinity of the species originating from CO₂RR while decreasing the competitive hydrogen evolution [40].

The present work follows our initial observation about possibility of electrochemical generation of nanostructured Pd⁰ within the coordination architecture of tridentate Schiffbase-ligands of the Pd^{II} -complex, $[Pd(C_{14}H_{12}N_2O_3)Cl_2]_2$ ·MeOH [27]. The Schiff base ligands with N,O-donors are employed in the metal-ion-directed assemblies of coordination architectures [41,42]. These ligands are fascinating and versatile complexing agents because their metal complexes are known to serve as luminescent probes [43], as catalysts in organic syntheses [44] and for specific DNA cleavage reactions [45], as well as in antibacterial [46] and anticancer [47] drugs. The well-defined Schiff base ligands containing nitrogen donor atoms are considered as 'privileged ligands' because of their capability to stabilize different metals in various oxidation states, and their complexes are extensively studied due to their synthetic flexibility, selectivity and sensitivity toward a variety of metal ions [48]. The structural diversity of palladium-driven polynuclear species [49] have permitted selfassembling supramolecular architectures of different nuclearity [50]. The palladium complexes with Schiff bases are known to exhibit high activities toward addition polymerization of norbornene [51], and to function as promising alternatives for phosphine/carbene species exhibit air and moisture stability and high catalytic activity in Heck reaction [52,53]. Furthermore, mononuclear complexes of Pd(II) ions with thiosemicarbazone ligands have been found to act as antitumour agents [54] or they show a groove binding mode to CT-DNA [55]. Following the successful synthesis of complexes of

Ag(I), Cu(II), Co(II) and Zn(II) [56] with ligand **L** (Figure 1), we have concentrated on the preparation of an analogous complex with palladium(II), initially with the metal-to-ligand (L) stoichiometry of 1:2 but, later, of the system containing only one molecule of ligand and two chloride ions [57-59]. Herein we explore a unique palladium complex with the characteristic N,N coordination mode:

To utilize the system in electrocatalysis, the Pd-complex has been deposited (by introducing the appropriate amount of its ink) onto the electrode surface and, subsequently, subjected to electroreduction through voltammetric potential cycling. In our preliminary communication [27], thus electrochemically-generated Pd⁰ nanocenters were demonstrated to exhibit reasonably high activity toward CO₂RR in near-neutral medium of CO₂-saturated KHCO₃. In this work, special attention is paid to physicochemical identity of the palladium complex (with its detailed crystallographic, IR and NMR features), electrochemical generation and characterization of Pd⁰ nanocenters, feasibility of stabilizing and activating interactions between Pd and N,N-coordination ligands, as well as to identification of the reaction products with the ultimate goal of explaining of high intrinsic catalytic activity of palladium supported within tridentate Schiff-base-ligand network. It is also reasonable to expect that, by formation and immobilization of Pd nanoparticles with supramolecular architectures of Schiff-base-ligands containing nitrogen donor atoms, the distribution and resistance to agglomeration of catalytic palladium should be improved. In comparison to conventional Pd nanoparticles, the performance of the Schiff-base-ligand-supported Pd nanoparticles is much higher during CO₂-reduction both under voltammetric and chronoamperometric conditions.

2. Experimental

2.1. Chemicals

All chemicals were commercial materials of analytical grade purity, except the palladium complex, which was synthesized according to the procedure described below. Pd black and 5wt% Nafion® perfluorinated resin solution were purchased from Sigma–Aldrich. Sulphuric acid, potassium bicarbonate and potassium formate were obtained from POCh (Gliwice, Poland) and Sigma–Aldrich.

Solutions were prepared using doubly distilled and subsequently de-ionized (Millipore Milli-Q) water. They were deoxygenated by bubbling with ultrahigh purified argon for 20 min prior to the electrochemical experiment. Measurements were made at room temperature $(22\pm2^{\circ}C)$.

2.2. Synthesis of palladium complex

The metal salts were used without further purification as supplied from Aldrich. The ligand L was prepared as described before [56]. NMR spectra were run on Varian Gemini 400 MHz spectrometer using TMS as an internal reference. Mass spectra for acetonitrile solutions ~10⁻⁴ mol dm⁻³ were determined using a Waters Micromass ZQ spectrometer. Sample solutions were introduced into the mass spectrometer source with a syringe pump at a flow rate of 40 μ dm³ min⁻¹ with a capillary voltage of +3 kV and a desolvation temperature of 300 °C. Source temperature was 120 °C. The cone voltage (V_c) was set to 30 V to allow transmission of ions without fragmentation processes. Scanning was performed from m/z = 200–1000 for 6 s, and 10 scans were summed to obtain the final spectrum. Microanalyses were obtained using a Perkin–Elmer 2400 CHN microanalyzer.

 $[PdLCl_2]_2$ ·MeOH. To the Schiff base ligand L (0.032 g, 0.125 mmol), first dissolved in 15 ml of MeOH, PdCl₂ was added (0.022 g, 0.125 mmol). Yellowish solution immediately turned red and solid of the same color precipitated. After 24 hours of stirring under ambient conditions, the precipitate was filtered, washed well with consecutively cold MeOH and Et₂O. Air drying gave 0.040 g of red complex with 73% yield. Single crystals suitable for X-Ray characterization were collected from the filtrate, upon slow evaporation of saturated methanolic/ether solution of the complex. ESI-MS(+): m/z (%) = 421 (100) {[PdLCl]·Na⁺}⁺, 361 (80) $[PdL]^+$, 833 (30) $[Pd_2L_2Cl_3]^+$. ESI-MS(-): m/z = 431 (100) $[PdLCl_2]^-$: IR (KBr): $v(O-H) = 3362, v(C-H)_{ar} = 3086, 3057, 3014, v_{as}(CH_3) = 2954, v_s(CH_3) = 2840, v_s(C=O) = 2840, v_s(O=O) = 2840, v_s$ 1702, ν (C=C)_{py} = 1624, 1596, 1584, 1562, 1542, ν (C=N)_{py} = 1491, 1485, 1432, ρ (C-H)_{py} = 1160, 1114, 1108, 1095, γ (C-H)_{pv} = 926, 906, 883, 828, 819, 765, 639, 548, 513 cm⁻¹; ¹H NMR (400 MHz, d₆-DMSO): $\delta = 8.80$ (s, 1H, H_a), 8.39 (dd, 1H, H_e, J¹ = 5.50Hz, J² = 1.20Hz, $J^{3} = 1.05Hz$), 8.21 (dt, 1H, H_c, $J^{1} = 7.83Hz$, $J^{2} = 1.51Hz$), 8.08 (d, 1H, H_b, $J^{1} = 1.96Hz$), 7.82 (dd, 1H, H_b, $J^1 = 7.81$ Hz, $J^2 = 1.05$ Hz, $J^3 = 0.90$ Hz), 7.69 (td, 1H, H_d, $J^1 = 5.58$ Hz, $J^2 = 1.05$ Hz, $J^2 = 1.$ 2.25Hz, $J^3 = 1.51Hz$), 7.64 (dd, 1H, H_f , $J^1 = 9.03Hz$, $J^2 = 1.96Hz$), 6.58 (d, 1H, H_g , J=9.03Hz), 3.80 (s, 3H, OMe) ppm. Analytical calculations: stoichiometric (%) for [Pd(C₁₄H₁₂N₂O₃)Cl₂]₂·MeOH (899.15): C, 38.74; H, 3.14; N, 6.23; found: C, 38.66; H, 3.25; N, 6.20.

X-Ray crystallography. Very thin red needles of the complex were obtained from the methanol/ether solution; X-ray diffraction data were collected at 130(1) K by the ω -scan technique on Agilent Technologies four-circle SuperNova diffractometer (Atlas detector) with mirror-monochromatized CuK_a radiation (λ =1.54178Å). The data were corrected for Lorentz-polarization and absorption effects [60]. Accurate unit-cell parameters were determined by a least-squares fit of 1068 reflections of highest intensity, chosen from the whole experiment. The structures were solved with SIR92 [61] and refined with the full-matrix least-squares procedure on F² by SHELXL97 [62]. Scattering factors incorporated in SHELXL97 were used. All non-hydrogen atoms were refined anisotropically, hydrogen atoms from O10-H groups were found in the difference Fourier maps and freely refined, all other hydrogen atoms were placed in the calculated positions, and refined as 'riding model' with the isotropic

displacement parameters set at 1.2 (1.5 for methyl groups) times the U_{eq} value for appropriate non-hydrogen atom.

Crystal data: 2(C₁₄H₁₂Cl₂N₂O₃Pd)·CH₃OH, M_r=899.15, monoclinic, P2₁, a= 14.1468(13)Å, b=7.7338(3)Å, c=15.818(2)Å, β=108.712(13)°, V=1639.1(3)Å³, Z=2, F(000)=892, d_x=1.82g·cm⁻³, μ (CuK_α)=12.30mm⁻¹, 6802 reflections collected, of which 4856 symmetry-independent (R_{int}=0.019), 4816 with I>2σ(I). Final R=0.045, wR2=0.127, S=1.06; max/min residual electron density in the final Δρ map: 1.25/-1.55 e·Å⁻³.

CCDC-**940669** contains supplementary crystallographic data for the complex. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

2.3. Electrochemical Measurements

All electrochemical measurements were performed with the use of CH Instruments 760E workstations in a three-electrode configuration. The reference electrode was a mercury/mercury sulfate electrode (Hg/Hg₂SO₄). All potentials are reported *vs*. Reversible Hydrogen Electrode (RHE). The gold rod was used as a counter electrode. The glassy carbon electrode served as the working electrode substrate. Before each modification, glassy carbon electrode was polishing with aqueous alumina slurries (grain sizes from 0.5 to 0.05 μ m) on a polishing cloth.

All electrochemical measurements were carried out in 0.1 mol dm⁻³ KHCO₃ solution under an atmosphere of Ar (pure, Air Products) or carbon dioxide (CO₂, 99.99 % Air Products).

2.4. Procedures involving Pd Nanoparticles

The suspension (ink) of the palladium complex was prepared as follows: a known amount (1.85 mg) of the palladium complex was dispersed in 100 μ dm³ of acetonitrile. Later 1,5 μ dm³ of the appropriate suspension was dropped onto the surface of a glassy carbon electrode by a micropipet. The resulting Pd-complex-layer was subjected to electroreduction through voltammetric potential cycling (25 full cycles at the scan rate of 50 mV s⁻¹) from 1.10 to -0.68 V (the latter potential value was sufficient to cause Pd^{II}-reduction and generate Pd⁰ sites) in the deoxygenated 0.1 mol dm⁻³ KHCO₃.

Comparative measurements were based on commercially available Pd nanoparticles. The respective aqueous suspension was prepared by dispersing (0.071 g) of palladium black in 2 cm³ of distilled water, followed by its sonication for 2 h. Later, the appropriate sample (2 μ dm³) was distributed over the glassy carbon electrode surface with a micropipet.

As a rule, the Pd-based catalytic films described above were covered with ultra-thin layers of Nafion polyelectrolyte by depositing 1 μ dm³ of the Nafion solution (prepared by introducing 5mass% of the commercial Nafion solution into ethanol at 1 to 10 volume ratio).

The loading of Pd in the catalytic layers (on glassy carbon) originating from both commercial Pd-black and Pd in Pd-complex was ca. 100 μ g cm⁻². Before measurements, the catalytic electrodes were conditioned by application of 25 voltammetric potential cycles at the 50 mV s⁻¹ scan rate between -0.68 V and 1.10 V in 0.1 mol dm⁻³ KHCO₃. Diagnostic cyclic voltammograms have been recorded at the scan rate of 10 mV s⁻¹.

The electrochemically active surface area (ECSA) of metallic palladium nanoparticles was estimated upon measuring the surface oxide reduction charge (from cyclic voltammetry). The data was normalized with respect to the active surface area. Knowing that the charge for the Pd-surface-oxide reduction (the Pd^{II} to Pd⁰ cathodic peak) in 1 mol dm⁻³ H₂SO₄ was reported to be equal to 424 μ C cm⁻² [36,37], the following ESCA values characteristic of tridentate-Schiff-base-ligand supported Pd nanostructures and conventional Pd nanoparticles

(deposited on glassy carbon) were estimated: 0.7 and 1.2 cm², respectively. Based on eight measurements, each performed following independent preparation of the respective Pd-containing systems, the reproducibility of the above determinations was on the level of 10% (standard deviation). Nevertheless, due to uncertainty of the assumed stoichiometry of Pd-oxide and unpredictable contribution from double layer charging, the above method is less reliable than that based on H-adsorption [36,37]; but the latter one is not applicable to metals (such as Pd) absorbing hydrogen.

2.5. IR measurements

Infrared spectra were recorded using the Nicolet iN10-MX-FTIR instrument (Thermo Scientific). The experiments were carried out in the reflectance mode and with use of MCT/A type detector. The sampled area was equal to $100 \ \mu m^2$. The spectral resolution was equal to $4 \ cm^{-1}$ and typically 16 scans were averaged for a single spectrum.

Thin layers of tridentate Schiff-base ligand, the ligand supported Pd nanostructures, and of the complex with palladium(II) were deposited on surface of the glassy carbon plate. The spectrum of the bare glassy carbon surface was considered as the background.

2.6. XPS measurements

XPS experiments were carried out using SPECS Surface Nano Analysis GmbH (Berlin, Germany) instrument equipped with XR 50 MF X-ray source and m-Focus 600 monochromator (600 mm Rowland Circle), using monochromatized X-ray Al Ka emission line, photon energy 1486.6 eV, operating at 120 W, and Phoibos 150 hemispherical analyzer with 150 mm radius, NAP version, equipped with 2D-DLD detector. The system base pressure was in the 10⁻¹⁰ mbar range. Spectra were fitted using CasaXPS software, version

2.3.17PR1.1 and the quantitative analysis were performed using CasaXPS built-in Scofield relative sensitivity factors.

2.7. Gas chromatographic analysis

Gas chromatograph (Agilent Technologies 7890A GC System) equipped with a silicabased Stationary Phase GS-GASPRO column, thermal conductivity detector (TCD) and flame ionization detector (FID) was used for analysis of gaseous products. Helium was used as the carrier gas; and sulfur hexafluoride (SF₆) as the internal standard.

3. Results and Discussion

3.1. Synthesis and characterization of Pd(II) Complex

Tridentate Schiff base ligand **L** was synthesized via typical condensation reaction between methyl 3-amino-4-hydroxybenzoate and picolinaldehyde as reported earlier [58]. The synthetic protocol applied to palladium(II) complex has intentionally omitted the use of external bases such as Et_3N , N_5 or AcO [57] thus aiming at exerting exclusive coordination of ligands nitrogen atoms and leaving aromatic hydroxyl group in its native form. Reaction of PdCl₂ with **L** ligand in equimolar ratio has resulted in formation of the complex in which N_2O -donor Schiff base coordinates the Pd(II) ion in bidentate mode to give the following formula: [PdLCl₂]. Electrospray mass spectrometry revealed the presence of peaks that correspond to [Pd(**L**)Cl₂]⁷, [Pd(**L**)]⁺ and [Pd(**L**)Cl]·Na⁺ species, which under ESI-MS conditions may associate to form [Pd₂(**L**)₂Cl₃]⁺. Nonetheless, isotopic distribution and spectrum as a whole (Fig. 2) does not give rise to other species than those M:L stoichiometry of 1:1. ¹H NMR studies of the complex in solution confirm that strictly mononuclear system is formed of the following formula [PdLCl₂].

The mononuclear form was retained in the solid state, as indicated by single crystal X-Ray studies, with additional MeOH molecule in the crystal lattice. It is interesting to note that no spontaneous deprotonation of phenolic OH group occurred, as for instance in complexes with the same ligand L [56] or similar ligands [58,59] where, without the need of exogenous base, formation of pseudo-grid dimers was observed. This fact was further corroborated by the IR spectrum (for simplicity not shown here), where broad band was found at 3362 cm⁻¹ which was ascribed to v(O-H) vibration. It should also be emphasized that aromatic ring with non-coordinating hydroxyl group was free to rotate, what is not out of significance when considering the surroundings of the palladium(II) ion and, indirectly, electrochemical behavior of palladium within [PdLCl₂] complex.

It is apparent from crystallographic data (available in *Supplementary Material*) that the structural unit in the crystal structure of the palladium complex consists of the fairlystrongly hydrogen-bonded two complex molecules and one solvent – methanol molecule (Figs S1 and S2). Geometrical parameters are summarized in Table S1. In the crystal structure (Fig. 3), there are some relatively short C-H···O hydrogen bonds joining the structural units. The hydrogen bond data are listed in Table S2. It should be emphasized that Pd(II) ions are fourcoordinated (by two ligand nitrogen and two chlorine atoms) in the square-planar environment which of importance to catalysis, including CO₂-reduction catalysis by tunable square-planar transition-metal complexes [2,4,6,8,10].

3.2. Electrochemical generation of Pd catalytic sites

To generate catalytic nanocenters within the palladium complex, a glassy carbon electrode modified with $[Pd^{II}(C_{14}H_{12}N_2O_3)Cl_2]_2$ ·MeOH (deposited as ink from suspension, according to the procedure described in Experimental section) has been subjected to 25 full voltammetric cycles (at 50 mV s⁻¹) in the potential range starting from 1.10 down to -0.68 V in the

deoxygenated 0.1 mol dm⁻³ KHCO₃ (Fig. 4). The lower potential limit has been chosen to be negative enough (-0.68 V) to assure reduction of Pd^{II} -sites (to Pd^{0}) within the complex layer. The increasing voltammetric peak currents, which have appeared during continuous voltammetric potential cycling (Fig. 4), should be correlated with hydrogen sorption (adsorption, absorption) and desorption phenomena (overlapping with hydrogen evolution at the negative potential limits) characteristic of the behavior of metallic palladium. are consistent with the formation of Pd^{0} catalytic centers. It is noteworthy that the stationary current responses have been obtained upon finalizing the voltammetric potential cycling. Although the latter observation does not mean complete transformation of Pd^{II} to Pd^{0} but it implies no futher electroreduction processes within the complex layer under experimental conditions of Fig. 4.

Based on structural information, dense crystal packing and existence of hydrogen bonds and multiple coordination planes (Figs S1, S2, S3 and S4; Tables S1 and S2), the electrochemically generated Pd⁰ centers should be distributed three-dimensionally within the rigid hydrogen-bonded network of supramolecular ligands. Having in mind the NMR spectrum of the original robust square-planar coordination architecture (Fig. 2), it is likely that the palladium sites are in the close vicinity of N-atoms originating from the nitrogencontaining ligands (Fig. 1).

3.3. Infrared characterization

The IR spectrum of the free ligand is shown in Fig. 5A (Curve a). The very broad band at 3369 cm⁻¹ originates from the O-H stretching motion of the phenyl group. The intense band at 1703 cm⁻¹ corresponds to the C=O stretching mode of the COOH group. The band at 1603 cm⁻¹ originates from the mixed contribution of the benzoic acid, pyridine ring deformation and the C=N stretching mode of the N=C bridge. The bands at 1521 and 1439 cm⁻¹ are

characteristic of the pyridine ring. The two bands at 1290 and 1208 cm⁻¹ are related to the C-N and C-C stretching of the imine group. The band at 1105 cm⁻¹ is related to the C-O stretching of the phenyl group.

Upon examination of the IR spectrum of the Pd(II)-complex (Fig. 5A, Curve b), it is apparent that the most noticeable change concerns the spectral range between 1300 and 1100 cm⁻¹. Obviously, upon formation of the Schiff base Pd(II)-complexes, both nitrogen atoms are involved in the coordination of the palladium ion. Furthermore, the O-H stretching band observed at 3369 cm⁻¹ in the ligand spectrum (Fig. 5A, Curve a) tends to disappear after the complexation (Curve b). The group of bands around 3000 cm⁻¹, which are visible in the spectrum of the complex, should be attributed to CH stretching modes. Most likely, these bands have been effectively covered by the broad O-H band in the free-ligand spectrum. The absence of the O-H in the Pd(II)-complex spectrum suggests that the phenol group is dissociated, and it presumably interacts with the positively charged palladium ion. The infrared spectra are consistent with the structure of the complex proposed on the basis of NMR results (Fig. 2).

The IR spectrum recorded following electrochemical generation of Pd⁰ centers within the complex (Fig. 5A, Curve c) shows that, in comparison to the untreated complex layer (Curve b), the main bands are not affected by the electrochemical treatment, thus indicating that the molecular structure of the supramolecular network of ligands is largely unchanged. There are, however, small differences in the spectral range below 1100 cm⁻¹. This range is dominated by the out-of-plane modes, which are sensitive to the conformation. The observed dissimilarity implies some alterations in the ligand conformation upon the change of the redox state of the palladium ion. On the whole, the geometry of the ligand seems to be unaffected upon electroreduction of the complex.

To get better insight into differences between the spectra of the complex before and after the reduction, we have enlarged the portions recorded in the 800 - 1050 (Fig. 5B) and 2800 - 3200 cm⁻¹ (Fig. 5C) ranges, respectively. First, the band at 980 cm⁻¹, which is characteristic of the Pd^{II}-containing complex, undergoes splitting after the electrochemical reduction. It can be postulated on the basis of studies with 4-hydroxybanzoic acid and pyridine [63,64] that the band at 980 cm⁻¹ (Fig. 5B, Curve b) comprises contributions from the out-of-plane C-H deformation modes of both aromatic rings of the ligand molecule. The splitting of this band implies changes in surroundings of the aromatic C-H groups upon the complex reduction. Another difference refers to the overlapping bands at 930, 914 and 905 cm⁻¹ (Fig. 5B, Curve b) which are transferred to two well separated bands at 926 and 905 cm⁻¹ after the complex reduction (Fig. 5B, Curve c). These bands are likely to stand for the out-ofplane deformation of the carbonyl (COOMe) group of the ligand (Fig. 1) and the out-of-plane modes of C-H [63,64]. But the most intense band of COOMe appears at 1703 cm⁻¹ (Fig. 5A, Curve a), and it does not change significantly upon the complex reduction (Fig. 5A, Curve c). Thus, it seems that the C-H groups are mostly affected by the reduction. Finally, while the band appearing at 2994 cm⁻¹ and corresponding to the C-H stretching modes have been observed for the Pd^{II}-complex (Fig. 5C, Curve b), they do not exit after the electroreduction (Fig. 5C, Curve c). These bands are likely to shift to higher frequencies and overlap with the neighboring band at 3120 cm⁻¹ (Fig. 5C, Curve c).

In conclusion, some electroreduction-induced reorganizations in the vicinity of aromatic C-H groups are apparent from the infrared data. They may reflect changes of dihedral angles between two aromatic rings of the ligand molecule as well as alterations of the C-H...O hydrogen bonding network. The presence of the C-H...O hydrogen bonds has already postulated on the basis of crystallographic data (*Supplementary Material*; Figs S1 and S2). But the original robust square-planar coordination architecture seems to be retained following electroreduction of the complex.

3.4. Microscopic examination

In our further studies aiming at physicochemical characterization and evaluation of performance of Pd⁰ nanocenters generated within tridentate-Schiff-base-ligand network, we have also considered conventional palladium black nanoparticles as the reference system. Morphologies (Fig. 6) of (a) pristine Pd(II) complex with tridentate-Schiff-base-ligands, (b) Pd nanostructures generated within the ligand network and (c) typical palladium nanoparticles have been examined using transmission electron microscopy (TEM). The data of Fig. 6b are consistent with the generation of Pd nanoparticles within the complex and formation of ligand-supported Pd nanoparticles (ligand-nPds). The sizes of ligand-nPds have been ranging from 5 to 10 nm. For comparison, the sizes of the commercial particles of palladium (nPds) have been on the level 15 nm. Both nanostructured catalytic materials tend to form agglomerates.

To get more information about morphology and composition of the films of Pd complex with tridentate-Schiff-base-ligands before and after the electrochemical generation of Pd^{0} catalytic sites, we have performed additional scanning electron microscopic (SEM) experiments. Fig. 7 illustrates SEM images of the films (deposited on glassy carbon) of (a) the

initial Pd(II) complex with tridentate-Schiff-base-ligands and (b) the system after electroreduction (by voltammetric potential cycling). The presence of palladium has been confirmed with surface microanalysis (EDS), and the existence of Pd is particularly evident from Pd-mapping images (white spots in images on the right in Figs 7a and 7b). The images of Fig. 7b are consistent with the formation (electrogeneration) of Pd nanoparticles or dendritic Pd⁰-nanostructures (ligand nPds) on surfaces or within the films initially deposited as elongated crystals of the Pd(II)-complex (Fig. 7a). The distribution of elements (carbon, nitrogen, palladium, chlorine palladium) oxygen, and in the complex layer $[Pd(C_{14}H_{12}N_2O_3)Cl_2)_2$ ·MeOH] has been before and after electrochemical reduction (Fig. 4). On the basis of the EDS analysis, it can stated that the amounts of palladium: in the reduced system and in the initial Pd(II)-complex are on the levels, 10.6 atomic% and 9.7 atomic%. In other words, the relative amounts of palladium before and after the electrochemical generation of Pd⁰ sites are comparable, and the observed difference may reflect the error of determination and local agglomeration of Pd centers upon reduction. The analytical data also imply the presence of carbon, oxygen, nitrogen and chlorine, as well as some potassium which originates from the supporting electrolyte (used for generation of ligand-nPds).

3.5. Electrochemical characterization

First, the electrochemical identity of palladium nanostructures generated within tridentate-Schiff-base-ligand network, was addressed the in such a model acid medium as deoxygenated 0.5 mol dm⁻³ H₂SO₄. Fig. 8 illustrates cyclic voltammograms recorded for ligand-nPds (red lines) in comparison to conventional nPds (black lines). As it is commonly accepted for the behavior of palladium nanoparticles, hydrogen sorption and desorption peaks (below 0.25 V) as well as responses characteristic of the Pd oxide formation and its reduction (above 0.55 V) appear in both cases (black and red lines) during voltammetric potential cycling in acid medium. Consequently, it is reasonable to postulate that Pd nanostructures

generated within tridentate-Schiff-base-ligand network exist in a form of metal nanoparticles, exhibit the interfacial redox processes characteristic of Pd^0 rather than the ionic-Pd-centered redox processes. In other words, the reduction of Pd^{II} -sites (within the complex) is in a sense irreversible: once Pd^0 centers are formed they behave like metallic palladium. Upon oxidation of Pd^0 sites, palladium oxides are generated, indeed, on their surfaces (Fig. 8) and, apparently, they are robust enough not to undergo complexation with the surrounding ligands. The latter statement is in agreement with the inorganic chemical properties of palladium [65].

To support our view that the electroreduction of Pd^{II} sites within the complex leads to the formation of Pd^{0} nanostructures, we provide an indirect proof by performing additional diagnostic experiments involving the electrocatalytic reduction of oxygen (the results are presented in *Supplementary Materials* in Fig. S5). It is well established that only metallic palladium centers are capable to effectively inducing reduction of oxygen (mostly to water) in acid medium [66]. Indeed, when the potential has been scanned negatively from 1.18 to 0.04 V, the characteristic O₂-reduction peak [66] has been observed at ca. 0.7 V for palladium electrogenerated within tridentate-Schiff-base-ligand network (Curve a in Fig. S5). If the ligand-supported-Pd-sites were ionic, the well-defined O₂-reduction voltammetric peak would be observed at more negative (than 0.7 V) potentials, i.e. until reduction of Pd^{II} -to- Pd^{0} sites occurs. Indeed, when the freshly prepared (not pre-reduced by voltammetric potential cycling) complex with Pd^{II} sites has been deposited on glassy carbon and subjected to the reductive voltammetric polarization in the presence of oxygen, the O₂-reduction peak has been shifted now to almost 0.4 V (Curbe b in Fig. S5) where catalytic Pd^{0} sites are electrogenerated.

Another important observation coming from the data of Fig. 8a is that (in the standard acid medium, 0.5 mol dm⁻³ H_2SO_4) the voltammetric responses of both ligand-nPds and conventional nPds are almost identical upon normalization of the voltammetric currents against the electrochemically active surface area (determined as described in Experimental

section). Thus, no significant structural differences are expected to exist between polycrystalline commercially available nPds and Pd nanostructures generated within supramolecular network. The close resemblance of responses characteristic of conventional nPds and ligand-nPds confirms once more that the electrogenerated palladium is predominantly in a form of Pd⁰ (rather than ionic Pd) sites. The fact that the current densities observed below 0.15 V are somewhat higher in the case ligand-nPds (Fig. 8a) may originate from more pronounced hydrogen adsorption capabilities of Pd nanostructures existing within the supramolecular network. The latter observation may reflect morphological differences between spherical-type conventional nPds and dendritic ligand nPds formed on surfaces or within eleongated crystals of the complex (Figs 6 and 7).

When the current densities are expressed against the geometric area of the glassy carbon electrode, the voltammetric responses would be quantitatively different for ligand-nPds (red lines) and nPds (black lines) (Fig. 8b). This result is consistent with the effectively lower electrochemically active surface area (ESCA) of ligand-nPds (ca. 0.7 cm²), relative to that characteristic of conventional nPds (ca. 1.2 cm²), despite the fact that the initial loading of 100 μ g cm⁻² was the same for Pd in both cases. It is reasonable to expect that, due to interactions with N,N coordination sites of supramolecular ligands, some portions of palladium surfaces in ligand-nPds have not been electroactive. Furthermore, although palladium nanostructures are characterized by the well-developed regions for the oxide monolayer formation and reduction, uncertainty of the present approach concerns mostly possibility of the formation of multilayer oxide films of undefined stoichiometry, in addition to unpredictability of double layer corrections which are likely to be dependent on morphology and degree of dispersion of Pd nanostructures. Thus, is spite of application of the analogous experimental conditions (same electrolyte and voltammetric polarization procedures), the obtained ESCA values should be considered as approximates.

3.6. XPS measurements

The analysis of surface layers of nPds, ligand-nPds, and the palladium complex was carried out by XPS experiment in order to obtain information about chemical nature and structure of the catalytic systems. The data of Figs 9a, 9b and 9c refer to the high-resolution XPS spectra of Pd 3d core level.

Based on the data obtained from XPS measurements for ligand-nPds and conventional-nPds (Figs 9a and 9b), two doublets are clearly visible in the spectra recorded in the Pd 3d region. First doublet (with the BE of Pd $3d_{5/2}$ component at 335.1 eV) corresponds to metallic palladium (about 55% for conventional nPds and 67% for ligand-nPds). But for conventional Pd nanoparticles, the second doublet (with the BE of Pd $3d_{5/2}$ at 336.8 eV) is located at the BE value characteristic of palladium(II) oxide (Fig. 9a). Interestingly, the Pd $3d_{5/2}$ signal of the second doublet (nonmetallic Pd) is located in the case of ligand-nPds at even higher BE of 338.2 eV (Fig. 9b); namely, at the value corresponding to the Pd $3d_{5/2}$ BE characteristic of the Pd(II) complex with tridentate Schiff-base ligand (Fig. 9c). Thus coordinative interactions with Pd(II) surface atoms can be envisioned. At the same time, the absence of the signal corresponding to palladium(II) oxides (compare Figs 9a and 9b) suggests that all oxidized Pd atoms are complexed by tridentate Schiff-base ligands, whereas the nanoparticle core retains its metallic (Pd⁰) character. The observed difference between the electronic properties of Pd(II) in the conventional nanoparticles and in the ligand nPds can be rationalized in terms of the contribution coming from the interactions of palladium with N,N coordination sites of supramolecular tridentate Schiff-base ligands.

3.7. Electrocatalytic CO₂-reduction

To get further insight into electrochemical behavior of tridentate-Schiff-base-ligand supported Pd nanoparticles (ligand-nPds; red lines), relative to the characteristics of conventional Pd nanoparticles (nPds; black lines), we have performed diagnostic cyclic voltammetric experiments in 0.1 mol dm⁻³ KHCO₃ electrolyte, i.e. in the supporting electrolyte used for electrocatalytic measurements (Fig. 10). The actual voltammetric responses have been recorded in the following potential ranges: (a) from 1.18 to -0.70 V, and (b) from 1.18 to -0.05 V. While the latter potential range (b) covers surface phenomena occurring on palladium at positive potentials (>0 V), the previous potential range (a) includes excursion toward more negative potential values (<0.2 V) where absorption of hydrogen is accompanied by hydrogen evolution. Here desorption of absorbed hydrogen takes place at potentials somewhat higher (ca. 0 V) that the onset potential characteristic of hydrogen evolution (ca. -0.3 V). In both cases (Figs 10a and 10b), hydrogen oxidation and desorption processes are evident during scanning potential from the negative limit toward positive values.

Upon medium transfer from H_2SO_4 (Fig. 8) to the near-neutral KHCO₃ solution (Fig. 5, Fig. 10a and 10b recorded in different potential ranges), such processes as the sorption of hydrogen (water reduction, or proton discharge, followed by hydrogen evolution) are kinetically less facile and the respective peaks are drawn out (Fig. 10a). Among important issues is the appearance of much higher hydrogen- sorption/hydrogen-evolution currents (<0.1 V) for the ligand-nPds (Fig. 10a, red line), in comparison to conventional nPds (Fig. 10a, black line). The coupled phenomenon of hydrogen oxidation and desorption appears in a form of the broad surface-type peaks in both cases (Fig. 10a) but, in the case of ligand-nPds (red line), at potentials more than 200 mV less positive, relative to conventional nPds (black line). Relatively low anodic currents starting at ca. 0.7 V (red line) and 0.85 V (black line) are consistent with the formation of thin oxide layers on surfaces of Pd nanoparticles. The

appearance of small cathodic peak at about 0.6 V (Fig. 10b) should be correlated with the reduction of previously generated (in anodic scans) Pd oxides. Finally, the hydrogen evolution starts in both cases at potentials below -0.45 V (Fig. 10).

As reported earlier, palladium exhibits electrocatalytic activity toward reduction of CO_2 [21-27]. The results of present studies (Fig. 11) indicate some differences in the performance of (a) conventional nPds, and (b) ligand-nPds. It is apparent upon comparison of responses in the presence (solid lines) and absence (dashed lines) of carbon dioxide that the onset potentials for CO_2RR can be correlated with the hydrogen evolution reaction regions characteristic of both types of Pd nanoparticles. The maximum current CO_2RR is attained at ca. -0.3 V on nPds (Fig. 11a) , and at -0.5 V on ligand-nPds (Fig. 11b). On the other hand, the onset potential for CO_2RR appears in the case of ligand-nPds at the less negative potential value of ca. -0.05 V (Fig. 11b), in comparison to -0.15 V characteristic of conventional nPds (Fig. 11a). What is even more important, is that the CO_2RR current densities (expressed against the electrochemically active surface area) are approximately five times higher for ligand-nPds (Fig. 11b), relative to the performance of conventional nPds (Fig. 11a). It is noteworthy that Pd-free tridentate-Schiff-base-ligands do not exhibit elctrocatalytic activity toward CO_2RR in the investigated range of potentials of Fig. 11.

Development of broad CO_2 -reduction peak (Fig. 11) reflects competition between the actual CO_2RR and evolution of hydrogen or absorption of hydrogen. It is reasonable to expect formation of CO-type poisoning species as the reaction products or intermediates. Judging from the observed much higher CO_2RR -current-denities, the degree of poisoning of surfaces of ligand-nPds is likely to be less pronounced in comparison to conventional nPds. It should

be remembered that hydrogen sorption/desorption phenomena seen to be more reversible ligand-nPds in comparison to conventional nPds (compare dashed lines in Figs 11a and 11b).

During positive potential scans recorded upon CO_2RR (solid lines in Fig. 11), the observed hydrogen oxidation currents are much less pronounced than those recorded in the absence of CO_2 (dashed lines in Fig. 11). The appearance of two anodic peaks at potentials higher than 0.5 V (solid lines in Fig. 11) should be correlated with the following phenomena: hydrogen desorption and oxidation of the CO_2 -reduction products (such as CO). The presence of the adsorbed CO_2RR products on Pd surface must have been responsible for the partial blocking of hydrogen desorption. The hydrogen oxidation peak is significantly shifted towards more positive values, and it seems to appear at potentials close to 1 V (i.e. following oxidative desorption of the poisoning CO-type reduction products).

3.7. Identification of CO₂RR products with gas chromatography

Gas chromatography was used for determination of volatile (gaseous) CO_2 reduction products obtained during CO_2RR performed at electrodes modified with conventional nPds and ligand-nPds. After 8 minutes of electrolysis under chronoamperometric conditions and application of different reduction potentials to the working electrode (the counter electrode was separated with Luggin capillary), the resulting 30 µl gas sample (taken with a GC injector from the gas collector) was mixed with 10 µl SF₆ and, then, injected into the gas chromatograph inlet. The gas collector was in the form of a funnel with a septum immersed in the electrolyte and placed directly above the GC electrode.

The results of gas chromatographic analysis are summarized in Table 1. Out of the selected electrolysis potentials applied to both catalytic electrodes, the relatively largest amounts of carbon monoxide (relative to hydrogen) have been obtained at the least negative potential of -0.82 V. In this respect (CO-generation), the system utilizing ligand-nPds seems

to be the most efficient, at the relative molar amounts of CO to H_2 are approximately 1:1. In other words, the electrochemical conversion of CO_2 into syngas becomes feasible under the above mentioned conditions.

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At potentials lower than -1.3 V, hydrogen evolution predominates over CO_2RR . The latter effect is even more sound at conventional nPds: at the potentials of -1.52 V and -1.72 V, no CO but only H₂ has been detected. Thus immobilization of palladium nanostructures within supramolecular network of tridentate-Schiff-base-ligands seems to affect selectivity of palladium and favors production of CO (over H₂).

3.8. Electrochemical characterization of CO₂RR products

Some information about the reaction products can be obtained from the stripping type electrochemical experiments [67-69] in which the oxidation voltammetric responses are recorded following application of different electroreduction potentials, E_{ad} 's (at which adsorption of the reaction products takes place). Before the linear scan (stripping) voltammograms have been recorded (Fig. 12), the Pd-containing catalytic electrodes have been for 1 s at the selected value of E_{ad} (from 0.18 V to -0.88 V). The reduction products have been formed and adsorbed on the electrode surface (in addition to simultaneous absorption of hydrogen on Pd). It was reported earlier that, by holding the catalytic (Pd) electrode at the potential of 0.50 V (Scheme 1), absorbed hydrogen was removed from Pd electrodes without oxidizing the adsorbed CO₂RR reduction. Following the suggested procedure [70], the potential has been maintained at 0.50 V for 3 s. Afterwards, the potential has been scanned (10 mV s⁻¹) toward positive values. This operation yields charge characteristic of the anodic oxidation of the adsorbed CO₂RR products (Q_{ECSA} ^{products}).

Figure 12 illustrates cyclic voltammetric responses measured for (a) conventional nPds and (b) tridentate-Schiff-base-ligand supported or ligand-nPds recorded following CO₂reduction (at different potentials under chronoamperometric conditions, as described above) in CO₂-saturated 0.1 mol dm⁻³ KHCO₃. The fact the voltammetric stripping peaks for the oxidation of the "reduced-CO₂" products (generated at different potentials) appear at potentials ca. 0.87-0.89 V is consistent with the surface oxidation of carbon monoxide as the predominant CO_2RR product.

The charge characteristic of stripping (oxidation) of "reduced-CO₂" (Fig. 12c) products provides important information about catalytic reactivity of conventional nPds and ligand-nPds. The relationship between the charge determined during oxidation of the adsorbed products generated during CO₂RR upon application of different E_{ad} potentials within the range from 0.60 to 1.20 V (Figs 12a and 12b) is shown in Fig. 12c. Upon decreasing E_{ad} potentials toward more negative values, magnitudes of charges related to the anodic oxidation of the adsorbed CO₂RR products (and normalized against the electrochemically active surface area, ECSA), Q_{ECSA}^{products}, which are initially (i.e., in the E_{ad} potential range from 0.2 to 0 V) equal to 0) tend to increase until the E_{ad} potential decreases to -0.6 V and, then, reaches plateau. An important issue is that, the determined values of charges are significantly higher for the Pd-catalyst immobilized within the supramolecular framework, in comparison to conventional Pd nanoparticles. Thus it is reasonable to expect that significantly larger amounts of CO-type products are generated when palladium exists within tridentate-Schiffbase-ligand network.

When CO_2RR is carried out on palladium catalyst in deoxygenated near-neutral aqueous solutions, carbon monoxide together with hydrogen are expected as reaction products but formation of formate is also feasible [21-26,71]. The appearance of carbon monoxide as the main CO_2RR product (at all reduction potentials considered in the present work) is evident form both gas chromatographic analysis and stripping type voltammetry (Fig. 12). Palladium is a very good catalyst for the oxidation of formic acid and formate, and its appearance as the CO_2RR product would contribute to the stripping-type voltammetric oxidation pattern. The blue curve in Fig. 13 illustrates a typical response for the electrooxidation of formate (in KHCO₃) recorded at ligand-nPds, whereas the black curve stands for the stripping peak

characteristic of the oxidation of the CO₂RR products (as in Fig. 12). The appearance of the single peak (stripping experiment) at about 0.87 V (black curve), namely without any shoulder at less positive potentials (as in the case of blue curve) implies that carbon monoxide has been the main reaction product. It is well established [33] that the oxidation of formic acid or formate proceeds at palladium largely without carbon monoxide intermediate, i.e. the onset for the formate oxidation is at less positive potentials as it is demonstrated in Fig. 13 (black curve). Judging from the data of Fig. 13, it can be concluded that, even if some formate is formed, the amounts are negligible relative to carbon monoxide appearing as the main reaction product at ligand-nPds.

3.8. Durability of electrocatalytic performance

The electrocatalytic stability (durability) of conventional nPds and ligand-nPds was addressed by performing chronoamperometric in CO₂.saturated 0.1 mol dm⁻³ KHCO₃ solutions upon application potential of the constant potential of -0.51 V for 1 h (Fig. 14). The initially-observed high currents reflect contributions originating from both the double-layer charging/discharging and the CO₂-reduction. The observed currents have decayed readily due to poisoning with CO-type reaction products. Finally, the currents reached the steady-state response after about 800 s. The existence of steady state currents implies that the system is well-behaved enough to be applicable to generate carbon monoxide and hydrogen (Table 1) through electrolysis. Furthermore, the steady-state currents are significantly (approximately two times) higher in the case of ligand-nPds, relative to the performance of conventional nPds.

Conclusions

Palladium nanoparticles, which are generated through electroreduction of palladium(II) ions in the complex with tridentate Schiff-base ligands, exhibit high activity toward CO₂RR in near-neutral medium of the CO₂-saturated KHCO₃. Both infrared and XPS results imply the existence of the largely unchanged square planar coordination architecture as well as the feasibility of stabilizing and, possibly, specific interactions of catalytic palladium centers with N,N coordination sites. The activating role of supramolecular ligand on Pd nanoparticles may involve not only complexing interactions or even changes in electronic nature of palladium catalytic centers (metal - support interactions) but also the ligand competitive role known as ,,third body" or steric effect [33]) with respect to partial removal of poisoning CO-type intermediates. When both voltammetric and chronoamperometric results have been normalized against the electrochemically active surface areas of Pd centers, the ligand-Pd system's performance has definitely been superior (larger current densities), in comparison to the conventional Pd nanoparticles. Based on chromatographic analysis and stripping type voltammetric experiments, carbon monoxide and hydrogen are the main reaction products. In other words, the proposed ligand-Pd-based catalytic system permits lowtemperature conversion of CO_2 and H_2O to syngas (CO + H_2), an useful intermediate for further Fischer-Tropsch processes.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by National Science Center (NCN, Poland) under Opus Project 2018/29/B/ST5/02627 (University of Warsaw) as well as partially under grant 2016/21/B/ST5/00175 (Adam Mickiewicz University, Poznan). The study has also been carried out in part at the Biological and Chemical Research Centre, University of Warsaw, established within the project co-financed by European Union from the European Regional Development Fund under the *Operational Program Innovative Economy*, 2007-2013.

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Fig. 1. Schematic representation of **L** ligand: (E)-methyl 4-hydroxy-3(pyridin-2-ylmethylneamino) benzoate.

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Fig. 2. ¹H NMR spectrum of the Pd(II) complex in aromatic region (6.5 - 9.0 ppm) with assignment of signals.

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Fig. 3. Crystal packing illustrated as seen along x-direction; hydrogen bonds are shown as dashed lines.

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Fig. 4. Cyclic voltammetric responses recorded during electrochemical generation of nPds within the tridentate-Schiff-base-ligand network (deposited on glassy carbon electrode). Electrolyte: 0.1 mol dm⁻³ KHCO₃. Scan rate: 50 mV s⁻¹.





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Fig. 5. (**A**) Infrared spectra of (a) free tridentate-Schiff-base-ligand, (b) the complex with palladium(II) ion, and (c) the complex with the generated Pd^0 sites. (**B**) and (**C**) illustrate the enlarged portions of the infrared spectra of (b) the complex with palladium(II) ion, and (c) the complex with generated Pd^0 sites in the 800 - 1050 and 2800 - 3200 cm⁻¹ ranges, respectively.



Fig. 6. TEM images of (a) pristine Pd(II) complex with tridentate-Schiff-base-ligands, (b) palladium sites generated within the complex (ligand-nPds), and (c) conventional Pd nanoparticles (nPds).

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Fig. 7. SEM images (on the left), corresponding EDX mixed elemental mapping of C, N, O, Pd, Cl (in the middle) and separate mapping image of Pd (on the right) of the following films (on glassy carbon electrode substrate): (a) the initial complex with palladium (II), and (b) tridentate-Schiff-base-ligand supported Pd nanostructures (obtained upon electroreduction by voltammetric potential cycling).



Fig. 8. Cyclic voltammetric responses of conventional Pd nanoparticles (black lines) and tridentate-Schiff-base-ligand-supported Pd nanostructures (on glassy carbon) (red lines) recorded deoxygenated in 0.5 mol·dm⁻³ H₂SO₄ solution. Scan rate: 10 mV s⁻¹. Current densities are expressed against (a) the electrochemically active surface area (ESCA) of Pd centers and (b) the glassy carbon electrode geometric surface area (geom).





Fig. 9. XPS Pd 3d spectra of (a) conventional Pd nanoparticles, (b) tridentate-Schiff-base-ligand supported Pd nanostructures, and (c) the palladium(II) complex.



Fig. 10. Cyclic voltammetric responses of conventional Pd nanoparticles (black lines) and tridentate-Schiff-base-ligand supported Pd nanostructures (red lines) recorded in deoxygenated 0.1 mol dm⁻³ KHCO₃ in different potential ranges: (a) down to -0.70 V and (b) down to -0.05 V. Scan rate: 10 mV s⁻¹. Current densities are normalized against the electrochemically active surface areas of Pd naoncenters.



Fig. 11. Cyclic voltammetric responses recorded for (a) conventional Pd nanoparticles, and (b) tridentate-Schiff-base-ligand supported Pd nanostructures (on glassy carbon) recorded in CO_2 -saturated (solid lines) and CO_2 -free (dashed lines) deoxygenated 0.1 mol dm⁻³ KHCO₃ solutions. Scan rate: 10 mV s⁻¹. Current densities are normalized against the electrochemically active surface areas of Pd nanocenters.





Fig. 12. Stripping voltammograms recorded at (**a**) conventional Pd nanoparticles and (**b**) tridentate-Schiff-base-ligand supported Pd nanostructures (on glassy carbon in CO₂-saturated 0.1 mol dm⁻³ KHCO₃. Scan rate: 10 mV s⁻¹. Plot (**c**) of anodic charges associated with the oxidation of the adsorbed products formed during CO₂-electroreduction upon application of different potentials (E_{ad}) to the conventional Pd nanoparticles (black circles) and tridentate-Schiff-base-ligand supported Pd nanostructures (red squares). The holding time was 1s.



Fig. 13. Comparison of the stripping voltammogram (recorded at 10 mV s⁻¹, following preconcetration at -0.5V for 1s) showing oxidation of the "reduced CO₂" (adsorbate) at tridentate-Schiff-base-ligand supported Pd nanostructures (black curve) to the voltammogram recorded for the oxidation (at 50 mV s⁻¹) of 25 mmol dm⁻³ formate (blue curve). Electrolyte: 0.1 mol dm⁻³ KHCO₃.



Fig. 14. Chronoamperometric curves of the conventional Pd nanoparticles (black line) and tridentate-Schiff-base-ligand supported Pd nanostructures (red line) recorded at -0.51 V in CO_2 -saturated 0.1 mol dm⁻³ KHCO₃.



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Scheme 1. Potential program for measuring CO₂RR products (adsorbates) on Pd through application of the anodic stripping step.

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Table 1. Formation of gaseous products upon application of different potentials to the conventional Pd nanoparticles (nPd's) and tridentate-Schiff-base-ligand supported Pd nanostructures (coordinated-nPd's).

E vs. RHE / V	nPd's		coordinated-nPd's	
	CO / %	H ₂ / %	CO / %	H ₂ / %
-0.82	46	54	49	51
-1.02	30	70	33	67
-1.12	26	74	28	72
-1.32	15	85	23	77
-1.52	0	100	20	80
-1.72	0	100	8	92

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