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Coordination properties towards palladium(II) of a tridentate dianionic ligand acting as a N- or a N,O-donor

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Abstract

The new palladium(II) complex Pd[C_5H_3N-2,6-$(CONPh)_2$](η^1-NCMe) (**1**), prepared from *N*,*N*′-diphenyl-2,6-pyridinedicarboxamide and $Pd(OAc)_2$ in acetonitrile, has been characterized via IR, ^1H NMR and single-crystal X-ray diffraction. In this compound the palladium centre is coordinated to three nitrogen donors of the anionic ligand and to the nitrogen atom of acetonitrile.

Moreover, the already known Pd[C_5H_3N-2,6-$(CONCH_2CH_2Ph)_2$](η^1-NCMe) (**2**) has been studied by ^1H NMR spectrometry and found to readily convert into the macrocyclic tetranuclear species **3**, {Pd[C_5H_3N-2,6-$(CONCH_2CH_2Ph)_2$]}$_4$ which has been isolated and characterized by IR, ^1H and $^{13}C\{^1H\}$ NMR, ^1H–^{13}C HETCOR and mass spectrometry, as well as by single-crystal X-ray diffraction. In **3**, of S_4 symmetry, each palladium atom is coordinated to the three nitrogen atoms of the anionic ligand, while the fourth coordination position is occupied by the amidato oxygen atom of an adjacent unit. This structure is apparently maintained in $CDCl_3$ solution. The substitution reactions of acetonitrile in **2** with the ligands EEt_2 (E = S, Se) afford Pd[C_5H_3N-2,6-$(CONCH_2CH_2Ph)_2$](EEt_2) (**4**, E = S; **5**, E = Se); these products can also be obtained by the addition of EEt_2 to **3**, as shown by means of ^1H- and, in the case of E = Se, $^{77}Se\{^1H\}$ NMR spectroscopy in $CDCl_3$ solution. These results show that the Pd–O bonds of the tetranuclear species are readily broken by weakly coordinating ligands such as acetonitrile and diethylchalcogenides. Nevertheless, we are dealing with equilibrium reactions and, in some solvents, **3** can be obtained from **2**, **4** or **5** being favoured by its low solubility.

Keywords: Palladium; Chalcogenoethers; Equilibrium study; X-ray

1. Introduction

As a further contribution to our studies on the stability of the metal–chalcogen bond [1], it appeared worthwhile to further explore the coordination properties of chalcogenoethers, by using palladium(II) as the metal acceptor. As a matter of fact, the coordination of selenoethers and telluroethers to transition metal complexes is a subject of renovated considerable interest [2].

In order to simplify the problem we wanted to possibly use a metal-containing precursor whereby one coordination position only could be substituted by the selected ligand. This restricted our choice to a tridentate di-anionic ligand. After an examination of the literature our choice was directed towards two specific compounds [3], namely *N*,*N*′-diphenyl-2,6-pyridinedicarboxamide ($dphpaH_2$) and *N*,*N*′-bis(2-phenylethyl)-2,6-pyridinedicarboxamide ($bphepaH_2$), the latter, see below, containing an ethylene bridge between the NH and the Ph groups [3a]. Both compounds are readily prepared and they had already been established to form the corresponding conjugate base upon double deprotonation.

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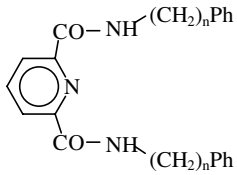
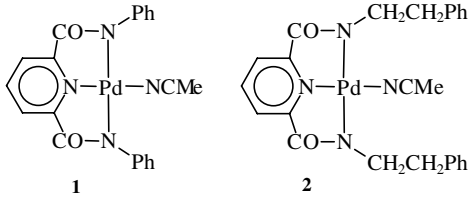
This was an important premise, as bivalent cations were expected, and had been established, to provide neutral complexes, presumably amenable to studies in organic solvent solution. Prior art in this field concerns the preparation of the iron(II) and cobalt(II) [3a] derivatives of both ligands and the crystal and molecular structure of the palladium(II) complex derived from bphepaH_2. Finally, palladium(II) was selected for this study in view of its well-established kinetic lability [4].



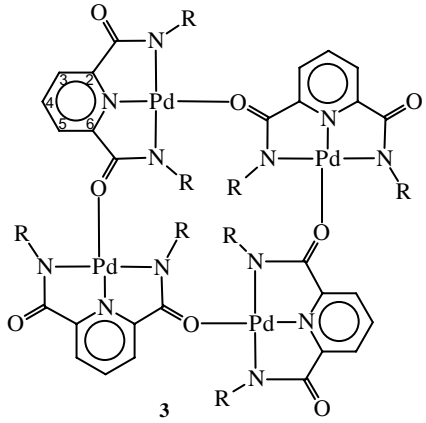
This paper reports the preparation and the crystal and molecular structure of the new compound (*N*,*N*′-diphenyl-2,6-pyridinedicarboxamidato) (η^1-acetonitrile)-palladium(II), **1**. The preparation of the more soluble already known [3b] [*N*,*N*′-bis(2-phenylethyl)-2,6-pyridinedicarboxamidato](η^1-acetonitrile)palladium(II), Pd(bphepa)(NCMe), **2**, evidenced that it easily loses MeCN and is converted to the MeCN-free tetranuclear derivative [Pd(bphepa)]$_4$, **3**, which has been studied both spectroscopically and crystallographically.



1 **2**

Thus, the carboxamidato group expands its coordination ability to the oxygen atom, thus leading to a remarkable molecular rearrangement. While this work was in progress the crystallographic data of another crystal modification of **3** have appeared [5].

The treatment of **2** or **3** with EEt_2 (E = S, Se) affords Pd(bphepa)(EEt_2) (**4**, E = S; **5**, E = Se).



3

R = CH_2CH_2Ph

2. Experimental

2.1. General

All manipulations were performed under an atmosphere of dry dinitrogen. Solvents were dried and distilled following standard procedures. Diethylsulfide (Merck, 98%) and diethylselenide (Aldrich) were used as received. Palladium(II) acetate [6], *N*,*N*′-diphenyl-2,6-pyridinedicarboxamide [3] and *N*,*N*′-bis(2-phenylethyl)-2,6-pyridinedicarboxamide [3] were prepared according to published procedures. Elemental microanalyses (C, H, N) were performed at Dipartimento di Scienze Farmaceutiche, Università di Pisa. IR spectra were recorded with a Perkin–Elmer Paragon 500 FTIR spectrophotometer. The NMR mono- and bidimensional spectra were recorded using a Varian-Gemini 200BB instrument, with the exception of the spectrum of **3**, which was measured with a Varian Inova 600 spectrometer. Chemical shifts δ are reported in ppm from TMS for ^{1}H and ^{13}C nuclei and from $SeMe_2$ for ^{77}Se. UV/Vis spectra were obtained with a Perkin–Elmer Lambda 9 spectrophotometer. DCI/MS spectra (positive and negative ions) were recorded with a magnetic double focalization reverse geometry Finnigan MAT 8400 spectrometer. One drop of a diluted $CHCl_3$ or CH_2Cl_2 solution of the sample was used to load the DCI wire. The DCI heating current was raised linearly to 1 A at a rate of 20 mA s^{-1}. Isobutane was employed as a reagent gas at a pressure of 0.2–0.3 mbar. In a typical experiment, the source was heated only by the 0.2 mA emission current of the filament (80–100 °C). The magnetic field was scanned in the range *m*/*z* 60–2000 at full (3 keV) accelerating voltage (*m*/Δm resolution, 2000; 10% valley). An upward quadratic scan of the magnetic field (1.3 s scan time; 1.5 s total cycle time) was adopted. Operating conditions of the ESI source positive ions/negative ions were as follows: spray voltage, 5–4 kV; capillary voltage 22 to −13 V; tube lens offset voltage −5 to −35 V; sheath gas (N_2), 50 units (roughly 1.25 L min^{-1}); capillary temperature, 200 °C. The sample, dissolved in CH_2Cl_2, or MeOH, or MeCN, was injected with a syringe pump at a flow of 5 μL min^{-1}. The instrument was operated from *m*/*z* 150 to 4000. ESI/MS spectra (positive and negative ions) were recorded with an ion-trap Finnigan LCQ spectrometer equipped with an ESI source and a syringe pump. Details of the experimental setup have been reported earlier [7a]. Mass-spectral data on compound **2** showed a main peak associated with a palladium-containing fragment at *m*/*z* 478 [corresponding to $(M - MeCN + H)^+$, both in $CHCl_3$ (DCI/MS, positive ions) and in MeCN (ESI/MS, positive ions)].

2.2. (*N,N′*-Diphenyl-2,6-pyridinedicarboxamidato)(η^1-acetonitrile)palladium(II), Pd(dphpa)(NCMe) (**1**)

N,N′-Diphenyl-2,6-pyridinedicarboxamide, dphpaH_2, (5 g, 15.8 mmol) was suspended in a solution of $Pd(OAc)_2$ (3.55 g, 15.8 mmol) in 1 L of acetonitrile. The resulting mixture was stirred for about 36 h, and the solvent was then removed in vacuo giving crude **1** (6.63 g, 91% yield) as a yellow-green solid, recrystallized as orange needles from acetonitrile. Elemental *Anal.* Calc. for $C_{21}H_{16}N_4O_2Pd$: C, 54.5; H, 3.5; N, 12.1. Found: C, 53.3; H, 3.6; N, 12.1%. IR (KBr, Nujol): 1616 cm^{-1}(ν_{CO}); (CD_3CN, CaF_2 cell): 1624 cm^{-1} (ν_{CO}). ^1H NMR (DMF-d_7) δ (ppm): 8.5–8.3 (m, py), 8.1–7.8 (m, py), 7.5–6.9 (m, 10H, arom.), 2.15 (s, 3H, MeCN). The DCI mass spectral data ($CHCl_3$ as solvent, positive ions) showed the main peak attributable to a palladium-containig fragment at *m/z* 422 [$(M - MeCN + H)^+$]. The ESI-MS data (MeCN, MeOH, positive ions) showed the main peak attributable to a palladium-containing fragment at *m/z* 462 $(M)^+$, 461 $(M - H)^+$, 485 $(MNa)^+$. The presence of MeCN was confirmed by the direct inlet probe Electron Ionization analysis (DIP/EI) at 70 eV.

2.3. Tetrakis{μ-[*N,N′*-bis(2-phenylethyl)-2,6-pyridinedicarboxamidato]}tetrapalladium(II), [Pd(bphepa)]$_4$ (**3**)

Compound **2** (0.419 g, 0.808 mmol) was refluxed in toluene (~200 mL) for ~4 h, followed by removal of the solvent in vacuo, addition of heptane (50 mL), and filtration of the resulting solid, which was dried in vacuo (0.174 g, 45% yield). The yellow solid is soluble in chloroform or dichloromethane, sparingly soluble in cold toluene and almost insoluble in heptane or hexane. Elemental *Anal.* Calc. for $C_{92}H_{84}N_{12}O_8Pd_4$: C, 57.8; H, 4.4; N, 8.8. Found: C, 56.9; H, 4.8; N, 8.4%. IR (KBr, Nujol): 1592 and 1551 cm^{-1} (ν_{CO}); (CH_2Cl_2, CaF_2 cell): 1598 and 1558 cm^{-1} (ν_{CO}). UV/Vis (1,2-dichloroethane): $\lambda_{max} = 275$ nm ($\varepsilon = 8900\ M^{-1}cm^{-1}$). ^1H NMR (600 MHz, $CDCl_3$): δ (ppm): 8.05 (t, $J = 7.8$ Hz, 4H, py), 7.85 (dd, $J = 7.8$ and 1.5 Hz, 4H, py), 7.43 (dd, $J = 7.8$ and 1.0 Hz, 4H, py), 7.25–7.10 (m, arom.), 6.93–6.92 (m, 12H, arom.), 6.83 (dd, $J = 7.5$ and 1.5 Hz, 8H, arom.), 5.92 (dt, $J = 7.5$ and 12.5 Hz, 4H, CH_2), 3.68 (ddd, $J = 12.5$, 10.0 and 5.5 Hz, 4H, CH_2), 2.99 (ddd, $J = 12.5$, 10.0 and 6.0 Hz, 4H, CH_2), 2.85 (ddd, $J = 13.0$, 10.0 and 5.5 Hz, 4H, CH_2), 2.66–2.49 (3 incompletely resolved ddd, 12H, CH_2), 2.36–2.30 (incompletely resolved ddd, 4H, CH_2). $^{13}C\{^1H\}$ NMR (200 MHz, $CDCl_3$, satd. soln.) δ (ppm): 169.4 and 169.1 (2 different CO), 154.2 and 152.4 [2 different C(py)–CO], 140.8 [C(py)–H], 140.3 and 138.0 [2 different C(Φ)–CH_2], 128.8, 128.5, 128.2, 128.1, 126.7, 125.9, 125.6 and 124.9 [2 different C(py)–H + C(Φ)–H resonances], 48.3, 47.4, 36.8 and 36.7 (4 different CH_2); ^1H-coupled-^{13}C NMR (200 MHz, $CDCl_3$) δ (ppm): 169.4 (CO), 154.2 and 152.4 [2 different C(py)–CO], 140.7 [C(py)–H, $J_{C-H} = 168$ Hz], 140.2 and 137.9 [2 different C(Φ)–CH_2], 132–123 [m, 2 different C(py)–H + C(Φ)–H resonances], 48.2 (t, $J_{C-H} = 137$ Hz, CH_2), 47.4 (t, $J_{C-H} = 139$ Hz, CH_2), 36.7 (t, $J_{C-H} = 129$ Hz, CH_2).

The ^1H–^{13}C HETCOR (200 MHz, $CDCl_3$) spectra, see Fig. 1, were obtained with the following acquisition parameters: delay 1 s, single acquisition time 0.079 s, overall acquisition time ~60 h).

Mass spectral data: main peak associated with a palladium-containing fragment at *m/z* 478 [corresponding to $(1/4M + H)^+$], both in CH_2Cl_2 (DCI or ESI/MS, positive ions) and in MeCN (ESI/MS, positive ions). Peaks of low intensity corresponding to $[(1/4M + Na) + (1/4M)_n]^+$ with $n = 1$–7 are present (ESI/MS, positive ions, MeCN as solvent).

2.4. Crystallographic study of compounds **1** and **3**

The X-ray diffraction experiments were carried out by means of a Bruker P4 diffractometer operating with graphite-monochromated Mo-K_α radiation. The intensities were measured with the $\omega/2\theta$ scan mode, collecting a redundant set of data. Three standard reflections were measured every 97 measurements to check sample decay. The intensities were corrected for Lorentz and polarisation effects and for absorption by means of a ψ-scan method [8]. The absorption correction was not applied to the intensities of compound **3**. The structure solutions were obtained by means of the automatic direct methods contained in SHELXS97 [9] for compounds **1** and SIR-92 [10] for compound **3**. The refinement, based on full-matrix least-squares on F^2, was done by means of the SHELXL97 [9] programme. Some other utilities contained in the WINGX suite [11] were also used.

A single crystal of **1** · MeCN was grown from acetonitrile and sealed in a Lindemann capillary under a dinitrogen atmosphere saturated with acetonitrile vapours. The structure solution of **1** was found in the non-centrosymmetric $Pna2_1$ space group. Besides the complex molecule, maxima corresponding to the heavy atoms of one acetonitrile lattice molecule were also found. The hydrogen atoms were in part located in the difference Fourier map and in part introduced in calculated positions. The final refinement cycle, performed with anisotropic thermal parameters for all the heavy atoms and constraining the hydrogen coordinates to 'ride' on the connected carbon atoms, gave the reliability factors listed in Table 1, along with other details concerning crystallographic data collection and structure determination.

Well -formed single crystals of **3** separated out from a $CDCl_3$ solution of the compound (about 0.1 M)

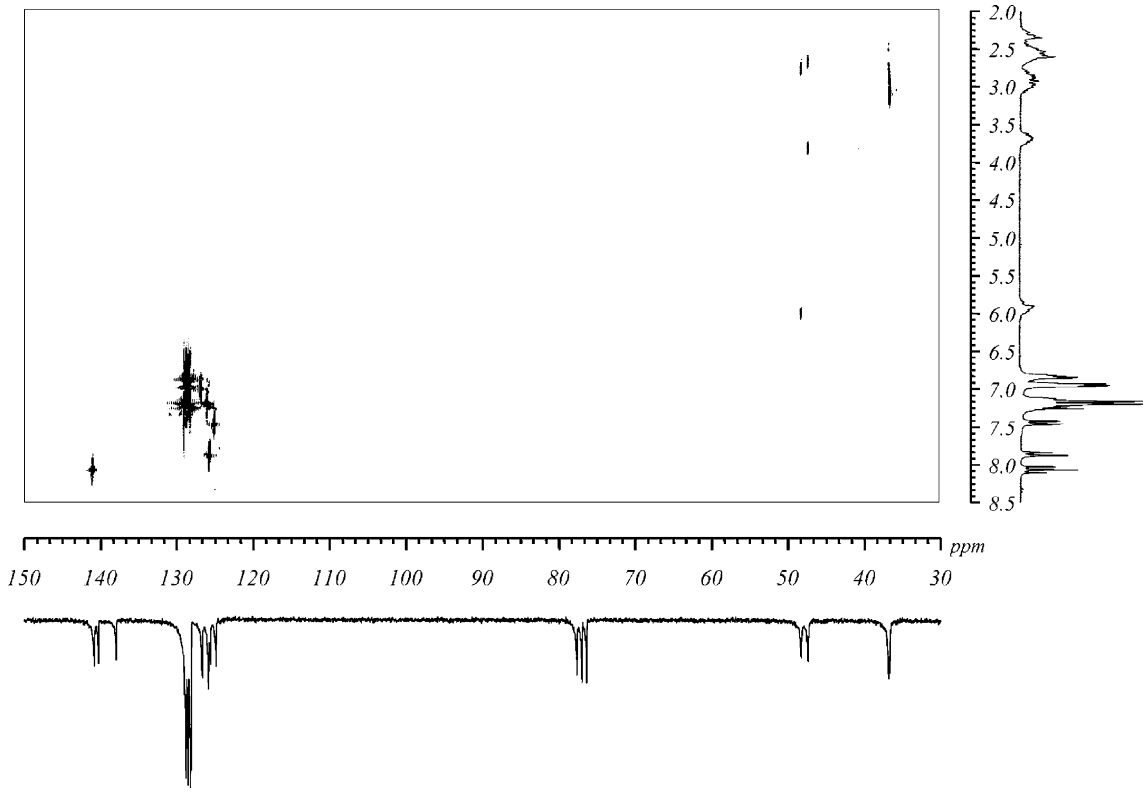


Fig. 1. ^{1}H–^{13}C HETCOR spectrum of **3** in $CDCl_3$ solution.

Table 1
Crystal data and details of the structure refinement for compounds **1** and **3**

	1 · MeCN	**3**
Formula	$C_{23}H_{19}N_5O_2Pd$	$C_{92}H_{84}N_{12}O_8Pd_4$
Formula weight	503.83	1911.31
Temperature (K)	298(2)	293(2)
Radiation λ (Å)	0.71073	0.71073
Crystal system	orthorhombic	tetragonal
Space group	$Pna2_1$ (no. 33)	$I\bar{4}$ (no. 82)
a (Å)	7.7043(8)	13.615(5)
b (Å)	15.072(2)	13.615(5)
c (Å)	18.268(2)	23.224(9)
Volume (Å^3)	2121.3(4)	4305(3)
Z	4	2
ρ_{calc} (Mg/m^3)	1.578	1.474
μ (mm^{-1})	0.905	0.885
Independent reflections [R_{int}]	2051 [0.0362]	2771 [0.0631]
Refined parameters	282	173
Goodness-of-fit[a] on F^2	1.106	1.062
R_1, wR_2 ($I > 2\sigma(I)$)[a]	0.0384, 0.1117	0.0588, 0.1515
R_1, wR_2 (all data)[a]	0.0515, 0.1190	0.0736, 0.1679

[a] $R(F_o) = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; $Rw(F_o^2) = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (AQ)^2 + BQ]$, where $Q = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$; GOF = $[\Sigma[w(F_o^2 - F_c^2)^2]/(N - P)]^{1/2}$, where N, P are the numbers of observations and parameters, respectively.

containing an excess of $SeEt_2$ (5:1), by vapour diffusion of pentane in the course of an attempt to obtain crystals of Pd(bphepa)($SeEt_2$), **5**. Structure solution was found in the non-centrosymmetric $I\bar{4}$ space group. The asymmetric unit corresponds to one fourth of the molecule, the whole frame being produced by the action of the $\bar{4}$ operator. Since the first stages of refinement, the abnormally high values of the thermal parameters of the benzyl moieties suggested the presence of disorder in these groups. Taking into account the direction of the longer axis of its prolated ellipsoids, the disorder was handled as they were distributed on two limiting positions. Each benzyl moiety was then refined as composed by two units with imposed hexagonal geometry and isotropic thermal parameters and fixing to 1 the total occupancy of the site. The hydrogen atoms were placed in calculated positions and refined with the above-mentioned riding condition. The reliability factors resulting from the final refinement cycle are listed in Table 1, along with other details concerning crystallographic data collection and structure determination.

2.5. [N,N′-bis(2-phenylethyl)-2,6-pyridinedicarboxamidato](diethylsulfide)palladium(II), Pd(bphepa)(SEt_2) (**4**)

Crystals of **4** were obtained by cooling to 4 °C a solution of **3** in SEt_2. The single crystal X-ray diffraction study showed that we were dealing with the title species. Although the crystallographic data are not of a high quality, they allowed the connectivity and the geometry of the

metal coordination sphere to be established. Structure solution was found in the $P\bar{1}$ space group. Cell parameters: $a = 13.334(5)$, $b = 13.662(5)$, $c = 16.312(5)$ Å; $\alpha = 88.07(5)$, $\beta = 89.25(5)$, $\gamma = 65.14(5)°$; $V = 2694.7(16)$ Å^3.

Attempts to set up a rational and high yield preparation of **4** produce samples containing **3** as an impurity.

2.6. [N,N′-bis(2-phenylethyl)-2,6-pyridinedicarboxamidato](diethylselenide)palladium(II), Pd(bphepa)($SeEt_2$) (**5**)

Compound **2** (0.842 g, 1.62 mmol) was dissolved in 10 mL of dichloromethane and $SeEt_2$ (0.5 mL, 4.50 mmol) was added. The mixture turned orange immediately after mixing. After stirring overnight, heptane (50 mL) was added, and the resulting suspension was filtered. The yellow solid was washed with heptane and dried in vacuo (0.803 g, 81% yield). Elemental *Anal.* Calc. for $C_{27}H_{31}N_3O_2PdSe$: C, 52.7; H, 5.1; N, 6.8. Found: C, 52.6; H, 5.1; N, 7.0%. IR (KBr, Nujol): 1595 cm^{-1} (ν_{CO}); ^{1}H NMR ($CDCl_3$) δ (ppm): 8.1 (t, $J \sim 7.5$ Hz, 1H, py), 7.8 (d, $J \sim 7.5$ Hz, 2H, py), 7.5–6.7 (m, arom.), 3.5 (br t, 4H, CH_2–N), 3.0–2.5 (m, 8H, CH_2–Φ + CH_2–Se), 1.5 (t, $J \sim 7.5$ Hz, 6H, CH_3 of $SeEt_2$). All resonances are rather broad. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ (ppm): 171.7 (CO), 151.2 (py), 141.0 (py), 140.1 (arom.), 128.7 (arom.), 128.3 (arom.), 126.0 (arom.), 124.4 (py), 49.8 (CH_2 of chelated ligand), 36.4 (CH_2 of chelated ligand), 23.8 (CH_2–Se), 14.6 (CH_3); $^{77}Se\{^1H\}$ NMR ($CDCl_3$): 244 ppm (versus $SeMe_2$). A ^{1}H NMR spectrum was measured on a $\sim 1.5 \times 10^{-3}$ M solution of **5** in $CDCl_3$. δ (ppm): 8.1 [m, pyridine (py) H of **5** and **3**], 7.9 (dd, $J = 7.8$ and 1.2 Hz, py of **3**), 7.8 (d, $J = 7.5$ Hz, py of **5**), 7.45 (dd, $J = 7.8$ and 1.2 Hz, py of **3**), 7.4–7.1 (m, arom. H of **5** and **3**), 6.95 (m, arom. H of **3**), 6.85 (m, arom. H of **3**), 5.95 (m, CH_2 of **3**), 3.7 (br, CH_2 of **3**), 3.5 (2 overlapping t, CH_2–N of **5**), 2.9–2.8 (m, CH_2–Φ + CH_2–Se of **5**), 2.6 (q, $J = 7.5$ Hz, CH_2 of free $SeEt_2$), 2.35 (br, CH_2 of **3**), 1.6 (t, $J = 7.5$ Hz, CH_3 of coordinated $SeEt_2$), 1.4 (t, $J = 7.5$ Hz, CH_3 of free $SeEt_2$).

In a control experiment, compound **2** (50 mg, 0.096 mmol) was dissolved in $CDCl_3$ (~0.5 mL, about 0.19 M)), $SeEt_2$ (~20 μL, 0.179 mmol) was added and a ^{1}H NMR spectrum was acquired after ~1 h. δ (ppm): 8.1 (t, $J = 7.7$ Hz, 1H, py), 7.8 (d, $J = 7.7$ Hz, 2H, py), 7.4–7.1 (m, 10H, arom.), 3.5 (2 overlapping t, 4H, CH_2–N), 2.9 (2 overlapping t, 4H, CH_2–Φ), 2.7 (br, 4H, CH_2–Se of both free and coordinated $SeEt_2$), 2.0 (s, 3H, MeCN), 1.5 (br t, $J = 7.3$ Hz, 6H, CH_3 of both free and coordinated $SeEt_2$). A $^{77}Se\{^1H\}$ NMR spectrum was also acquired. δ (ppm): 244 (free $SeEt_2$), 227 (coordinated $SeEt_2$).

The interaction of the tetranuclear compound **3** with $SeEt_2$ was also studied. Compound **3** (39.7 mg, 0.083 mmol Pd) was dissolved in $CDCl_3$ (0.5 mL), diethylselenide (13.9 μL, 0.12 mmol) was added and a ^{1}H NMR spectrum was recorded after ~3 h. δ (ppm): 8.1 (t, $J = 7.7$ Hz, 1H, py), 7.8 (d, $J = 7.7$ Hz, 2H, py), 7.4–7.1 (m, 10H, arom.), 3.5 (2 overlapping t, 4H, CH_2–N), 2.9 (2 overlapping t, 4H, CH_2–Φ), 2.75 (br, CH_2–Se–Pd), 1.5 (br t, CH_3 of $SeEt_2$). A $^{77}Se\{^1H\}$ NMR spectrum was also recorded. δ (ppm): 244, 227.

3. Results and discussion

3.1. Compound **1**

When an acetonitrile solution of $Pd(OAc)_2$ was treated with an equimolar amount of *N*,*N*′-diphenyl-2,6-pyridinedicarboxamide, $dphpaH_2$, palladium(II) coordinates to the corresponding diamidato dianion, affording complex **1** as for Eq. (1).

$$Pd(OAc)_2 + dphpaH_2 + MeCN \rightarrow \underset{\mathbf{1}}{Pd(dphpa)}(NCMe) + 2HOAc \quad (1)$$

By removing the volatiles in vacuo, the crude product was obtained, which was recrystallized from acetonitrile as yellow-orange needles, sparingly soluble in almost all organic solvents except *N*,*N*-dimethylformamide and acetonitrile. The solid-state IR spectrum of the product shows a C=O stretching band at 1616 cm^{-1}, which is ~40 cm^{-1} lower than that of $dphpaH_2$. The ^{1}H NMR spectrum of **1** (recorded in DMF-d_7 solution), contains two sets of resonances between 8.5 and 7.8 ppm and between 7.5 and 6.9 ppm, due to the pyridine protons and to the phenyl protons, respectively. A singlet at 2.15 ppm is ascribed to the methyl group of free acetonitrile, suggesting that DMF displaces acetonitrile from the coordination sphere of palladium.

A schematic drawing of the solid-state structure of **1**, derived from X-ray diffraction data on a single crystal of **1** · MeCN, is reported in Fig. 2, some relevant bond distances and angles are listed in Table 2.

The palladium coordination environment is approximately square-planar. The N(2) atom exhibits the maximum deviation (0.0542 Å) from the best plane. The metal centre is 0.0224 Å away from this plane on the opposite side with respect to N(2). The Pd–N(3) and Pd–N(4) distances range between 1.96 and 2.04 Å, which are expected values for square-planar palladium(II) to this type of ligands [12]. The N(2) atom is 1.953(8) Å away from the metal centre: comparatively short Pd–N(py) bonds have been reported [12,13] for palladium(II) square-planar complexes having a similar structure, e.g., $[Pd(MeCN)(pybox)](BF_4)_2$ [13], (pybox = 2,6-bis[4′-(*S*)-phenyloxazoline-2′-yl]pyridine) where the Pd–N(py) distance is 1.927(7) Å. The N(1)–Pd–N(3) angle of **1** is 159.5(3)°, while the N(2)–Pd–N(4) angle is 176.0(3)°. Analogous departures from the ideal

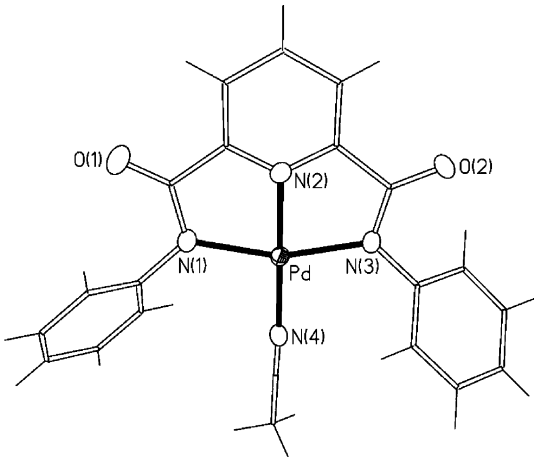


Fig. 2. View of the molecular structure of **1.** Thermal ellipsoids are at 30% probability.

Table 2
Selected bond distances (Å) and angles (°) for compound **1**

Pd–N(1)	2.076(8)
Pd–N(2)	1.953(8)
Pd–N(3)	2.040(8)
Pd–N(4)	2.017(9)
N(1)–Pd–N(2)	79.4(3)
N(2)–Pd–N(3)	80.2(3)
N(4)–Pd–N(3)	100.2(3)
N(4)–Pd–N(1)	100.3(3)

square-planar geometry have been reported [14] for similar complexes.

Finally, it should be noticed that the phenyl groups form a dihedral angle of ~50° with the average coordination plane of palladium, thus presumably minimizing the steric hindrance. A similar phenomenon occurs in $[Pd(MeCN)(pybox)](BF_4)_2$, where the corresponding dihedral angles are 79° and 76° [13]. In complex **1**, Pd–N distances and N–Pd–N angles are analogous to the corresponding metrical parameters of complex **2** [15].

3.2. Compound 3

The already known compound **2** was also studied because it was considered that the ethylene chain interposed between the nitrogen atom and the phenyl group on passing from **1** to **2**, could modify the properties, for instance the solubility, of the palladium(II) precursor. The new findings largely met these expectations: **2** shows a high solubility for instance in aromatic hydrocarbons or chloroalkanes. Nevertheless we have found that, in solution, **2** is in equilibrium with the tetranuclear species **3** according to Eq. (2).

Compound **3** was prepared by refluxing **2** in toluene, followed by removal of the volatiles, acetonitrile included, under reduced pressure.

$$4\underset{\mathbf{2}}{Pd(bphepa)}(NCMe) \rightleftharpoons [\underset{\mathbf{3}}{Pd(bphepa)}]_4 + 4MeCN \quad (2)$$

In the course of this work we found that solutions of other adducts of the type Pd(bphepa)L ($L = SEt_2$, $SeEt_2$) separate **3** with release of free L, as we discuss later on. Actually, the most beautiful single crystals of **3** were grown, in an attempt to obtain crystals of Pd(bphepa)($SeEt_2$), from a ~0.1 M solution of **3** in $CDCl_3$, in the presence of excess $SeEt_2$ (molar ratio Se/Pd ~ 5), by slow diffusion of pentane vapors. The crystals of the tetranuclear complex **3** separated out, presumably due to its low solubility.

Two different projections of the molecular structure of **3**, which crystallizes in the tetragonal system, are shown in Fig. 3. The more relevant bond lengths and angles are listed in Table 3.

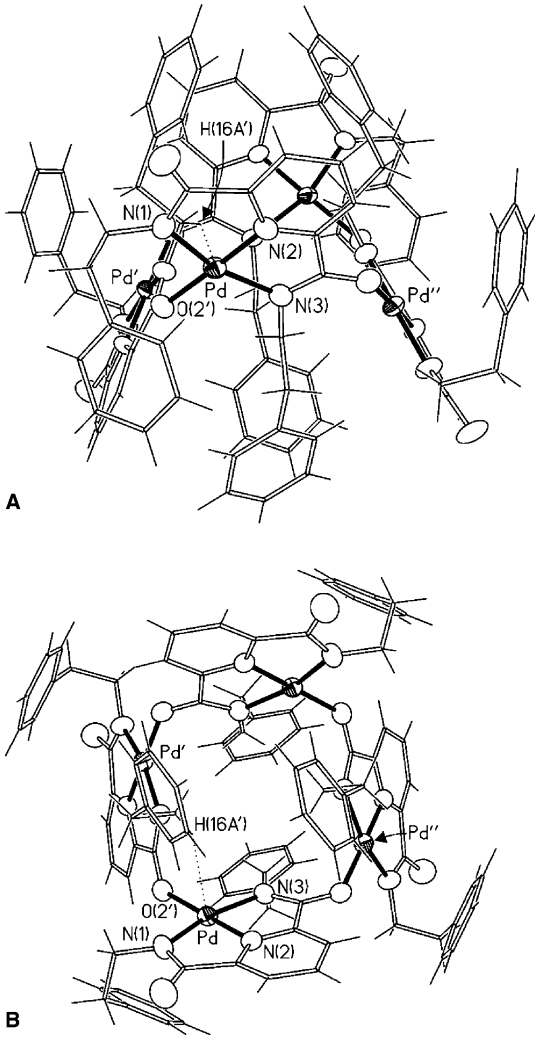


Fig. 3. Two projections of the molecular structure of **3**: A, perpendicular, and B, parallel to the $\bar{4}$ axis. Only the most populated positions of the disordered benzyl groups are shown. Thermal ellipsoids are at 30% probability. Dotted line shows the short Pd···H(16A′) distance, 2.539 Å. $' = 1 - y, x, 2 - z$, $'' = y, 1 - x, 2 - z$.

Table 3
Selected bond distances (Å) and angles (°) for compound **3**

Pd–N(1)	2.008(9)
Pd–N(2)	1.908(8)
Pd–N(3)	2.042(9)
Pd–O(2′)	2.017(9)
N(1)–Pd–N(2)	82.0(4)
N(2)–Pd–N(3)	80.2(4)
O(2′)–Pd–N(1)	97.6(4)
O(2′)–Pd–N(3)	100.3(3)

The apex has the same meaning as in Fig. 3.

While this work was in progress, a paper appeared [5] describing another crystal modification of compound **3**. In our modification the four palladium atoms in the molecule are equivalent by $\bar{4}$ (S_4) symmetry. The already known phase of **3** crystallizes in the triclinic $P\bar{1}$ space group without symmetry elements relating parts of the molecule.

The molecular structure of the triclinic modification ($\mathbf{3}_{tricl}$) is essentially analogous to that of the tetragonal one ($\mathbf{3}_{tetr}$), as for the Pd–N distances [Pd–N(py) = 1.913(9) Å for $\mathbf{3}_{tricl}$, 1.908(8) Å for $\mathbf{3}_{tetr}$; ⟨Pd–NCO⟩ = 2.03(1) Å for $\mathbf{3}_{tricl}$, 2.025(6) Å for $\mathbf{3}_{tetr}$] and N–Pd–N angles [OCN–Pd–NCO = 161.3(4)° for $\mathbf{3}_{tricl}$, 162.1(4)° for $\mathbf{3}_{tetr}$] within each mononuclear unit. The Pd–N lengths fall within the range of 1.91–2.06 Å, which is normal for palladium(II) square-planar complexes [12]. Significant differences are observed between the two crystalline phases. The difference in the Pd–O distances, 2.064(8) Å for $\mathbf{3}_{tricl}$ and 2.017(9) Å for $\mathbf{3}_{tetr}$, is more than five times the standard deviation. Being the Pd–O bond the hinge which joins the four {Pd[C_5H_3N-2,6-$(CONPh)_2$]} moieties, we suppose that the tetragonal arrangement allows a better disposition of the whole molecule, producing a slightly stronger Pd–O bond. Both crystal structures exhibit a nearly square-planar coordination geometry for each palladium atom.

However, the major difference between the triclinic and the tetragonal phases is the orientation of the terminal benzyl groups, which are easily visualized by superimposing the two molecular structures. A detailed analysis of this subject should include the disorder of the benzyl groups in the tetragonal phase, which is beyond the scope of this report.

Compound **3** was studied via NMR in chloroform solution. The 600 MHz ^{1}H NMR spectrum in $CDCl_3$ (see Fig. 1 and Supplementary Material) is consistent with the solid-state structure of Fig. 3, taking into consideration that the S_4 symmetry axis passing through the centre of the macrocycle makes the palladium-containing units equivalent to one another, and that each methylene group bears diastereotopic protons, consistent with the absence of symmetry planes.

Moreover, the phenylethyl protons located in the inner part of the $(\cdots O{=}C{-}N{-}Pd\cdots)_4$ macrocycle, will not be equivalent to those in the periphery of the molecule. In addition, as free rotation about the $CH_2{-}\Phi$ bond is reasonably assumed, the *ortho*-protons will give rise to a single peak, and the same applies to the *meta*-protons.

Moreover, the 8.05 ppm triplet is assigned to the pyridine proton in 4-position (cfr. 8.1 ppm for **2**); the two double doublets at 7.85 and 7.43 ppm, respectively, correspond to the other two pyridine protons (cfr. the doublet at 7.5 ppm for **2**). Further, there are a multiplet at 7.25–7.10 ppm, and a couple of signals at 6.92 and 6.83 ppm, respectively. Both the multiplet and the latter two resonances integrate for five protons (by assuming the integral of the 8.1 ppm triplet as the unit), and arise from the two unequivalent aromatic nuclei. For comparison, in complex **2** the protons of the two aromatic nuclei (therein equivalent to one another) originate one resonance around 7.2 ppm. Finally, there are eight structured signals between 5.92 and 2.30 ppm (each of them is a doubled double doublet, and some of them are not well-resolved), each of which integrates for one proton. Each of these resonances can be ascribed to one of the eight non-equivalent methylene protons on the pendant phenylethyl groupings. Each resonance is structured because each methylene proton couples with the geminal one, as well as with each proton on the adjacent methylene group. The spectrum computed (LEQUOR program [16]) by using the spectral parameters reported in the experimental part gives an excellent fit to the experimental one.

The resonance centred at 5.92 ppm shows a remarkable downfield shift with respect to the corresponding resonances of **2**, located at 3.35 and 2.75 ppm. Such a shift may be explained taking the solid-state structure of **3** into consideration: it is seen (Fig. 3) that the H(16A′) proton is 2.57 Å away from the palladium atom (Pd in the figure) belonging to the contiguous unit, the Pd–H(16A′) vector being almost orthogonal to the coordination plane. Based on literature [17,18], the H(16A′) proton is shifted downfield due to paramagnetic anisotropy arising from Pd. This hypothesis is consistent with the van Vleck's theory, which states that a weak paramagnetism can be induced by external magnetic fields on atoms whose d orbitals are not completely filled, and whose fundamental-state total spin quantum number equals 0, such as palladium(II) (d^8). The $^{13}C\{^1H\}$ NMR spectrum of **3** can be interpreted similarly to the ^{1}H NMR spectrum. A bidimensional ^1H–^{13}C HETCOR spectrum of complex **3**, see Fig. 1, confirmed the proton couplings.

To conclude, NMR data are consistent with the solid-state structural data of tetragonal modification of **3**. It should be noticed that the triclinic crystal modification reported in the literature [5], when in solution, would be expected to give NMR spectra more complicated than those previously discussed. As a matter of fact, the palladium-containing units of the triclinic

modification are not equivalent, since the S_4 symmetry element is absent.

In the ESI/MS [7] mass spectra of **3**, recorded by using a CH_2Cl_2 solution, the most intense peak is due to the palladium-containing mononuclear unit (*m/z* 476 for negative ions and 478 for positive ions), as the result of the tetranuclear structure undergoing fragmentation. This kind of cleavage, involving Pd–O=C bonds, is consistent with the well-established [19] low stability of this type of bonds.

It should be noted that the ESI/MS spectra of **2** show the most intense fragment at *m/z* 477 (negative ions) and 478 (positive ions). The agreement with the mass spectra of **3** can be accounted for by postulating that the Pd–NCMe bond of **2** breaks up on ionization, in keeping with the rather low stability of Pd–NCMe bonds reported in the literature [20].

3.3. Reactivity of compounds 2 and 3 with EEt_2 (E = S, Se)

We have observed that products **2** and **3** interact with the diethylchalcogenides EEt_2 (E = S, Se) to afford the complexes **4** and **5** according to equilibria (3)–(6).

$$\mathrm{Pd(bphepa)(NCMe)_{2} + SEt_2} \rightleftharpoons \mathrm{Pd(bphepa)(SEt_2)_{4} + NCMe} \quad (3)$$

$$1/4[\mathrm{Pd(bphepa)}]_{4\,(3)} + \mathrm{SEt_2} \rightleftharpoons \mathrm{Pd(bphepa)(SEt_2)_{4}} \quad (4)$$

$$\mathrm{Pd(bphepa)(NCMe)_{2} + SeEt_2} \rightleftharpoons \mathrm{Pd(bphepa)(SeEt_2)_{5} + NCMe} \quad (5)$$

$$1/4[\mathrm{Pd(bphepa)}]_{4\,(3)} + \mathrm{SeEt_2} \rightleftharpoons \mathrm{Pd(bphepa)(SeEt_2)_{5}} \quad (6)$$

The ^{1}H NMR spectrum of the reaction mixture between **2** and SEt_2 in the molar ratio 1:1, showed a quartet and a triplet at 2.7 and 1.5 ppm, respectively, assigned to the methylene and the methyl protons of coordinate SEt_2. These resonances were accompanied by weak signals, assigned to uncomplexed diethylsulfide at 2.6 and 1.3 ppm. Resonances at 2.15 and at 2.0 ppm were assigned to coordinated and uncomplexed acetonitrile, respectively. These findings agree with the presence in solution of equilibrium (3) involving the formation of the diethylsulfide adduct, **4**. From the ratio between the integrals of the resonances at 2.0 and 2.15 ppm, an equilibrium constant *K* of about 15 was estimated. Thus, the Pd–SEt_2 bond appears to be slightly more strong than the Pd–NCMe bond [20]. Product **4** can be obtained also by reacting **3** with an excess of SEt_2. Crystals of **4** separated out by a solution obtained by adding **3** to neat SEt_2 when it was stored at about 4 °C. It is interesting to note that attempts to separate pure solid **4** from its solutions (in $C_nH_{2n+2-x}Cl_x$) by addition of a hydrocarbon as pentane or by evaporation of the solvent met with some difficulties because of the competing precipitation of **3**, observed even in the presence of an excess of SEt_2.

As far as the reaction of $SeEt_2$ with **2** is concerned, when a molar ratio of about 2 between the reagents was employed: the ^{1}H NMR spectrum of the reaction mixture showed the resonance at 2.0 ppm due to uncomplexed acetonitrile, but no signal attributable to coordinate MeCN. Therefore, in these conditions the equilibrium involving **2** and $SeEt_2$ (see Eq. (5)) appears to be almost totally shifted to the right. ^{77}Se{^{1}H} NMR spectrum of the mixture exhibited two signals at 228 and 244 ppm, respectively, the former due to uncoordinated $SeEt_2$, the latter being attributed to ligated $SeEt_2$. The downfield shift of 16 ppm of coordinated $SeEt_2$ is rather modest; however it is in the range of those reported in the literature [21,22]. It is interesting to point out that in the ^{1}H NMR spectrum only one set of rather broad signals due to $SeEt_2$ was observed [at 2.7 (q) and 1.5 (t) ppm], suggesting that free and coordinate ligands undergo rapid exchange on the NMR time scale. The apparent contrast between the ^{77}Se- and ^{1}H NMR data can be settled by considering that the greater difference in chemical shift of selenium signals, with respect to hydrogen, will correspond to an enhancement of the coalescence temperature. The presence of well separate signals due to the free and coordinate thio-ether in the ^{1}H NMR spectrum of solutions containing **4** and SEt_2 could be explained with a slower ligand exchange rate, which well agrees with the different kinetic constants measured for substitution reactions in platinum(II) complexes, SeR_2 being better nucleophiles than SR_2 [23].

The diethylselenide adduct **5**, as prepared from **2** and $SeEt_2$ in dichloromethane solution, can be obtained pure in the solid state by addition of heptane in the presence of an excess of $SeEt_2$, to avoid the concomitant precipitation of the tetranuclear derivative **3**. The formation of **3** is clearly bound to the set up of equilibrium (6) in solution, the slight solubility of this tetranuclear species causing its prompt precipitation.

4. Conclusions

The complex Pd(bphepa)(NCMe), **2**, used in this work as precursor to study the relative stability of the derivatives Pd(bphepa)(ER_2) (E = S, Se), releases acetonitrile in solution, being in equilibrium with [Pd(bphepa)]$_4$, **3**, which shows low solubility in hydrocarbons. Both the complexes, **2** and **3**, react with EEt_2 (E = S, Se) with formation of Pd(bphepa)(EEt_2): in all cases

equilibria are involved, the palladium centre preferring in the order $SeEt_2$, SEt_2, $NCCH_3$ and at the end the oxygen atom of one amido group of another Pd(bphepa) fragment. Although the oxygen-donor ligand appears to be the weakest one, it becomes the compulsory choice when the solubility limit of **3** is reached.

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Appendix A. Supplementary data

Crystallographic data for compounds **1** and **3** have been deposited in the form of CIF files with the Cambridge Crystallographic Data Centre CCDC reference numbers 271557 and 271558, respectively. Copies of the data may be obtained free of charge, on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033, email: deposit @ccdc.cam.ac.uk or on the web www: http://www.ccdc.cam.ac.uk. The experimental and the LEQUOR computed ^{1}H NMR spectrum are also available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2005.06.073.

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