Available online at www.sciencedirect.com
SCIENCE DIRECT®
Inorganica Chimica Acta 359 (2006) 127–135
Inorganica Chimica Acta
www.elsevier.com/locate/ica

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

Daniela Belli Dell'Amico [a,*], Fausto Calderazzo [a], Francesco Di Colo [a], Gianfranco Guglielmetti [b], Luca Labella [a], Fabio Marchetti [a]

[a] *Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, I-56126 Pisa, Italy*
[b] *Polimeri Europa, Istituto "G. Donegani", Via G. Fauser 4, I-28100 Novara, Italy*

Received 26 May 2005; accepted 13 June 2005

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**, $\{Pd[C_5H_3N\text{-}2,6\text{-}(CONCH_2CH_2Ph)_2]\}_4$ 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].

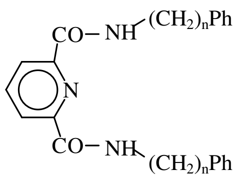
In order to simplify the problem we wanted to possibly use a metal-containing precursor whereby one coordination position only could be substituted by the selected ligand. This restricted our choice to a tridentate di-anionic ligand. After an examination of the literature our choice was directed towards 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.

---

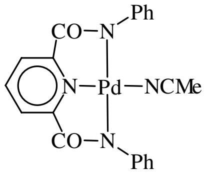
[*] Corresponding author. Tel.: +39 050 2219 206; fax: +39 050 2219 246.
E-mail address: belli@dcci.unipi.it (D. Belli Dell'Amico).

0020-1693/$ - see front matter
doi:10.1016/j.ica.2005.06.073

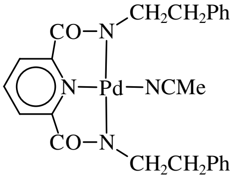
This was an important premise, as bivalent cations were expected, and had been established, to provide neutral complexes, presumably amenable to studies in organic solvent solution. Prior art in this field concerns the preparation of the iron(II) and cobalt(II) [3a] derivatives of both ligands and the 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.



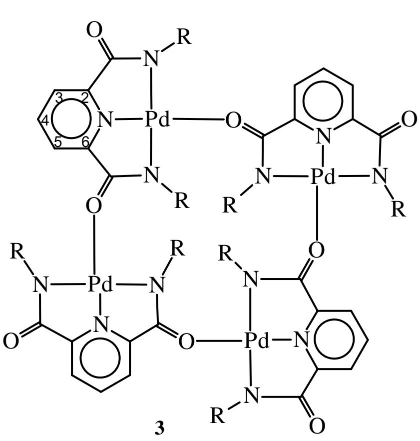
1



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 ^1H 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 ($m/\Delta m$ 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)].