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Synthesis and Characterization of Metallocyclic Complexes of Palladium(II) with Monoalkyl (α-Anilino-*N*-benzyl)phosphonates

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The synthesis, spectroscopic and thermal properties of the novel five-membered [N,O] metallocyclic complexes of palladium(II) with monoethyl (H**L1**) and monobutyl (H**L2**) esters of (α-anilino-*N*-benzyl)phosphonic acid are reported. Binuclear complexes Pd_2L_4 (L = **L1**, **L2**) were obtained by reaction of sodium salts of monoalkyl phosphonates with $PdCl_4^{2-}$ in aqueous solution. Four organophosphorus ligands bridge two palladium atoms by coordination through the aniline nitrogen and the deprotonated phosphonic acid oxygen. The complexes were identified and characterized by elemental analysis, magnetic and conductance measurements, as well as by spectroscopic (ESI-MS, IR, UV-VIS, ^{1}H and ^{31}P NMR) and thermal (TG, DTA) studies. The properties of the complexes are discussed with respect to those of palladium(II) metallocyclic complexes reported for monoalkyl 4-azobenzene-substituted anilinobenzylphosphonates.

Key words: palladium(II) complex, metallocycle, sodium anilinobenzylphosphonate, aminophosphonate complex, spectroscopy, thermal decomposition.

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INTRODUCTION

Studies of metallocyclic complexes of palladium(II) with nitrogen donor ligands are of current interest owing to their wide-range application in organic synthesis and catalysis.[1,2] Recently, these compounds have been studied also with regard to their biological and toxicological properties.[3,4] Specific interest in this field has been directed towards derivates of aminocarboxylic and aminophosphonic acids because of their relevance to the natural systems and potential biological activity.[5–9] Following our interest in the study of palladium(II) complexes with alkyl esters of various aminophosphonic acids, especially of those which might be of interest as anticancer agents,[8–13] in the present report we describe the synthesis as well as spectroscopic analyses and decomposition properties of new metallocyclic dipalladium(II) complexes, Pd_2L_4, of monoethyl (H**L1**) and monobutyl (H**L2**) esters of (α-anilino-*N*-benzyl)phosphonic acid. Ligand coordination through the aniline nitrogen and the phosphonic acid oxygen occurs in the basic media where the phosphonic acid group is deprotonated. In the course of investigation, the results obtained were compared with those obtained earlier for the corresponding [N,O] palladium(II) chelates of monoalkyl [4-α-(benzeneazoanilino)-*N*-benzyl]phosphonates.[13] It was found that these organophosphorus ligands form mononuclear metallocyclic complexes, PdL_2, under the same reaction conditions. Spectral and thermal properties of the complexes are discussed in terms of their structure-stability relationship.

EXPERIMENTAL

Materials

Sodium salts of monoethyl (Na**L1**) and monobutyl (Na**L2**) ester of (α-anilino-*N*-benzyl)phosphonic acid, prepared according to known procedures by alkaline hydrolysis of the corresponding dialkyl phosphonates,[14] were purified by repeated recrystallizations from absolute ethanol and dried by heating to about 50 °C under high vacuum. All other reagents and solvents were analytical grade products and were used without purification.

*Sodium monoethyl (α-anilino-*N*-benzyl)phosphonate (Na**L1**)*

M.p. 230–232 °C; UV-VIS ($CHCl_3$) λ_{max}/nm (log ε): 289 (3.37); IR (KBr) ν_{max}/cm^{-1}: 1606s, 1500vs, 1463m-s [ν(C=C), δ(N–H)], 1220vs, 1201vs [$\nu_{as}(PO_2^-)$], 1094sh, 1076vs br, 1042vs, 1030sh [$\nu_{sym}(PO_2^-)$, ν(PO–C)]; ^{1}H NMR (DMSO–d_6) δ/ppm: 0.93 (t, 3H, J_{HH} = 7.1 Hz, CH_3), 3.53 (q, 2H, $J_{HH} = J_{PH}$~7.0 Hz, OCH_2), 4.25 (dd, 1H, J_{HH} = 7.1, J_{PH} = 22.0 Hz, PC*H*), 5.59 (dd, 1H, J_{HH} = 6.0, J_{PH} = 10.0 Hz, N*H*), 6.40 (t, 1H, J_{HH} = 7.0 Hz, H-4), 6.53 (d, 2H, J_{HH} = 8.3 Hz, H-2,6), 6.91 (t, 2H, J_{HH} = 7.7 Hz, H-3,5), 7.05 (t, 1H, J_{HH} = 7.0 Hz, H-10), 7.16 (t, 2H, J_{HH} = 7.3 Hz, H-9,11), 7.37 (d, 2H, J_{HH}=7.3 Hz,

H-8,12); Negative-ion ESI-MS (MeOH, 30 eV) m/z (%): $[(NaL1)_2–Na]^-$ 603 (8), $[L1]^-$ 290 (100).

Anal. Calcd. for $C_{15}H_{17}NO_3PNa$ (M_r = 313.26): C 57.51, H 5.47, N 4.47, P 9.89%; found: C 57.74, H 5.68, N 4.29, P 9.78%.

Sodium monobutyl (α-anilino-N-*benzyl)phosphonate (Na**L2**)*

M.p. 179–181 °C; UV-VIS ($CHCl_3$) λ_{max}/nm (log ε): 289 (3.39); IR (KBr) ν_{max}/cm^{-1}: 1604vs, 1521m, 1500s, 1453m [ν(C=C), δ(N–H)], 1218vs, 1190s [$\nu_{as}(PO_2^-)$], 1084vs, 1076vs br, 1068vs, 1031s [$\nu_{sym}(PO_2^-)$, ν(PO–C)]; ^{1}H NMR (DMSO–d_6) δ/ppm: 0.77 (t, 3H, J_{HH} = 7.0 Hz, CH_3), 1.04–1.42 (m, 4H, CH_2CH_2), 3.49 (m, 2H, OCH_2), 4.22 (dd, 1H, J_{HH} = 6.0, J_{PH} = 21.3 Hz, PC*H*), 5.50 (br s, 1H, N*H*), 6.48 (t, 1H, J_{HH} = 7.2 Hz, H-4), 6.52 (d, 2H, J_{HH} = 8.0 Hz, H-2,6), 6.93 (t, 2H, J_{HH} = 6.8 Hz, H-3,5), 7.07 (t, 1H, J_{HH} = 6.7 Hz, H-10), 7.17 (t, 2H, J_{HH} = 7.0 Hz, H-9,11), 7.36 (d, 2H, J_{HH} = 6.3 Hz, H-8,12); ^{31}P NMR ($CDCl_3$) δ/ppm: 23.25; Negative-ion ESI-MS (MeOH, 30 eV) m/z (%): $[(NaL2)_2–Na]^-$ 659 (5), $[L2]^-$ 318 (100).

Anal. Calcd. for $C_{17}H_{21}NO_3PNa$ (M_r = 341.32): C 59.82, H 6.20, N 4.10, P 9.08%; found: C 59.72, H 6.48, N 4.29, P 9.18%.

μ-Tetrakis[monoethyl (α-anilino-N-*benzyl)phosphonato]dipalladium(II) (**1**)*

A concentrated aqueous solution of $K_2[PdCl_4]$ (0.110 g, 0.34 mmol) was added dropwise to a stirred solution of Na**L1** (0.185 g, 0.59 mmol) in water (5 mL). The reaction mixture was continuously stirred at room temperature for 4 h. The pale yellow precipitate formed was filtered off, washed with cold water and dried under vacuum over P_2O_5 for 24 h. Yield 0.185 g (91%); UV-VIS ($CHCl_3$) λ_{max}/nm (log ε): 286 (3.84); IR (KBr) ν_{max}/cm^{-1}: 1601m, 1495m, 1451w-m [ν(C=C), δ(N–H)], 1238m-s, 1215vs [$\nu_{as}(PO_2^-)$], 1075m, 1046s, 1027s, 995vs [$\nu_{sym}(PO_2^-)$, ν(PO–C)]; ^{1}H NMR ($CDCl_3$) δ/ppm: 1.11 (br s, 3H, CH_3), 3.80 (br s, 2H, POCH_2), 4.80 (br s, 1H, PC*H*), 6.20–8.10 (br m, 11H, Ar*H*, N*H*); Negative-ion ESI-MS (MeOH, 30 eV, ion masses referenced to isotope ^{106}Pd) m/z (%): $[M\text{-}H]^-$ = $[Pd_2(L1)_4–H]^-$ 1373 (3), $[Pd(L1)_3]^-$ 976 (9), $[Pd(L1)_2–H]^-$ 685 (5), $[L1]^-$ 290 (100).

Anal. Calcd. for $C_{60}H_{68}N_4O_{12}P_4Pd_2$ (M_r = 1373.88): C 52.45, H 4.99, N 4.08, P 9.02, Pd 15.49%; found: C 52.35, H 4.73, N 4.65, P 9.05, Pd 15.79%.

μ-Tetrakis[monobutyl (α-anilino-N-*benzyl)phosphonato]dipalladium(II) (**2**)*

This complex was prepared by the same procedure as complex **1** by reaction of Na**L2** (0.250 g, 0.73 mmol) and $K_2[PdCl_4]$ (0.160 g, 0.49 mmol) in water (5 mL). Yield 0.210 g (78%); UV-VIS ($CHCl_3$) λ_{max}/nm (log ε): 286 (3.99); IR (KBr) ν_{max}/cm^{-1}: 1600w-m, 1491m, 1455w-m [ν(C=C), δ(N–H)], 1240sh, 1227vs br [$\nu_{as}(PO_2^-)$], 1067m, 1028s, 1010vs, 1000s [$\nu_{sym}(PO_2^-)$, ν(PO–C)]; ^{1}H NMR ($CDCl_3$) δ/ppm: 0.65 (br s, 3H, CH_3), 1.14,1.36 (two br s, 4H, CH_2CH_2), 3.70 (br s, 2H, POCH_2), 4.85 (br s, 1H, PC*H*), 6.10–8.30 (br m, 11H, Ar*H*, N*H*); ^{31}P NMR ($CDCl_3$) δ/ppm: 23.25, 26.19, 27.55, 28.51, 30.19, 34.20; Negative-ion ESI-MS (MeOH, 30 eV, ion masses referenced to isotope ^{106}Pd) m/z (%): $[M\text{-}H]^-$ = $[Pd_2(L2)_4–H]^-$ 1485 (2), $[Pd(L2)_3]^-$ 1060 (4), $[Pd(L2)_2–H]^-$ 741 (3), $[L2]^-$ 318 (100).

Anal. Calcd. for $C_{68}H_{84}N_4O_{12}P_4Pd_2$ (M_r = 1486.08): C 54.96, H 5.70, N 3.77, P 8.34, Pd 14.32%; found: C 54.72, H 5.73, N 3.49, P 8.48, Pd 14.59%.

Physical Measurements and Analyses

Infrared spectra were recorded on a Perkin-Elmer 580 B spectrophotometer using KBr pellets. Ultraviolet-visible spectra were measured in chloroform solution with a Perkin-Elmer 124 spectrometer in the range 250–600 nm. Electrospray ionization mass spectrometric (ESI-MS) measurements were performed on a Navigator (Finnigan, San Jose, CA, USA) instrument equipped with an ESI ion source. Complexes were investigated in negative ion mode with different cone voltages (30, 50 and 120 V), using methanol as the solvent and mobile phase. ^{1}H NMR spectral analyses were performed with Varian Gemini 300 and Bruker AMX 360 spectrometers. Spectra were recorded in $CDCl_3$ and DMSO-d_6 containing $SiMe_4$ as an internal standard, as described in our previous studies.[13] ^{31}P NMR spectra were measured at 145.79 MHz on a Bruker AMX 360 spectrometer in $CDCl_3$ with external 85% H_3PO_4 in a coaxial capillary.

Thermogravimetric analyses (TG) were carried out on a Cahn RG electromicrobalance in an air atmosphere at a heating rate of 4 °C min^{-1} up to 860 °C. Differential thermal analyses (DTA) were performed with a Netzsch differential thermal analyzer applying a heating rate of 5 °C min^{-1} in a static air atmosphere. The X-ray powder diffraction patterns were taken with a Philips counter diffractometer (monochromatized Cu–Kα radiation). Melting points were determined on a hot stage microscope and are uncorrected. Conductance measurements were carried out at room temperature using a CD 7A Tacussel conductance bridge for 10^{-3} mol L^{-1} solutions in DMF. Magnetic susceptibilities in the solid state were measured at room temperature by the standard Gouy method using a Cahn-Ventron RM-2 balance and $CuSO_4 \cdot 5H_2O$ as susceptibility standard. Elemental analyses (C, H, N) were performed in the Microanalytical Laboratory of the Ruđer Bošković Institute.

RESULTS AND DISCUSSION

Sodium salts of monoalkyl (α-anilino-*N*-benzyl)phosphonic acid (Na**L1** and Na**L2**), similarly to sodium monoalkyl [4-α-(benzeneazoanilino)-*N*-benzyl]phosphonates,[13] give, by reaction with $PdCl_4^{2-}$ in water (M:L = 1:2), [N,O] chelate complexes with ligand bonded through the aniline nitrogen and the phosphonic acid oxygen. While benzeneazoanilino derivatives give mononuclear PdL_2 metallocyclic complexes, anilinobenzylphosphonates form binuclear Pd_2L_4 complexes (Figure 1). The prepared complexes are microcrystalline pale yellow compounds, stable under normal laboratory conditions, insoluble in water and slightly soluble in common organic solvents. Their diamagnetic behaviour suggests square-planar stereochemistry around palladium(II) ions. The very low molar conductance values (below 1 S cm^2 mol^{-1} in DMF) confirm the presence of deprotonated phosphonic acid groups in the complexes. The structure of complexes as well as their stability and mode of decomposition were deduced from their spectroscopic (ESI-MS, IR, UV-VIS, ^{1}H and ^{31}P NMR) and thermal (TG, DTA) studies.

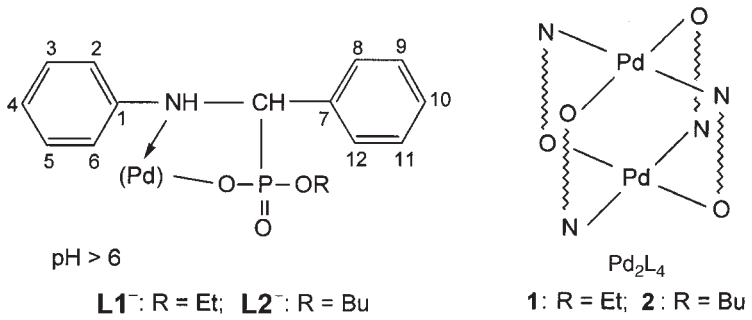

Figure 1. Proposed chemical structure and numbering scheme of palladium complexes with monoalkyl (α-anilino-*N*-benzyl)phosphonates.

Spectroscopic Studies

Mass Spectra

The negative-ion ESI-mass spectrometric investigations of palladium complexes **1** and **2** gave valuable structural information about these compounds. The results obtained reveal formation of binuclear tetrakis(anilinobenzylphosphonato)dipalladium(II) complexes. It may be presumed that two palladium atoms are N,O-bridged by four organophosphorus ligand molecules. The deprotonated molecular ion $[(Pd_2L_4)–H]^–$ of *ca*. 3% relative intensity was observed at *m/z* 1371 and 1485, respectively. Structure-specific fragment ions are formed by the loss of one palladium and one ligand molecule as well as by the loss of one palladium and two ligand molecules from the parent complex ion, giving the mononuclear palladium fragment ions $[PdL_3]^–$ and $[(PdL_2)–H]^–$, respectively. The molecular ion as well as fragment ions containing palladium are identified by the presence of characteristic clusters of isotopic peaks covering about 10 *m/z* units, due to the presence of numerous palladium isotopes (Figure 2). The predominant pathway for fragmentation of complexes is the dissociation of phosphonate ligand molecules. The deprotonated ligand ion $[L]^–$ is the major and the only intense fragment ion in the spectra of complexes, as well as in the sodium monoalkyl anilinobenzylphosphonates Na**L1** and Na**L2**. Dimerization of the sodium salt molecules gives rise to $[(NaL)_2–Na]^–$ ions at *m/z* 603 and 659, respectively.

It is worth noting that in the case of previously reported mononuclear benzeneazoanilinophosphonate complexes the relative intensity of the deprotonated molecular ion $[(PdL_2)–H]^–$ is very small, up to 1%,[13] indicating less stability of these compounds compared to the binuclear anilinobenzylphosphonate complexes. It may be presumed that dimerization contributes to the stabilization of binuclear complexes.

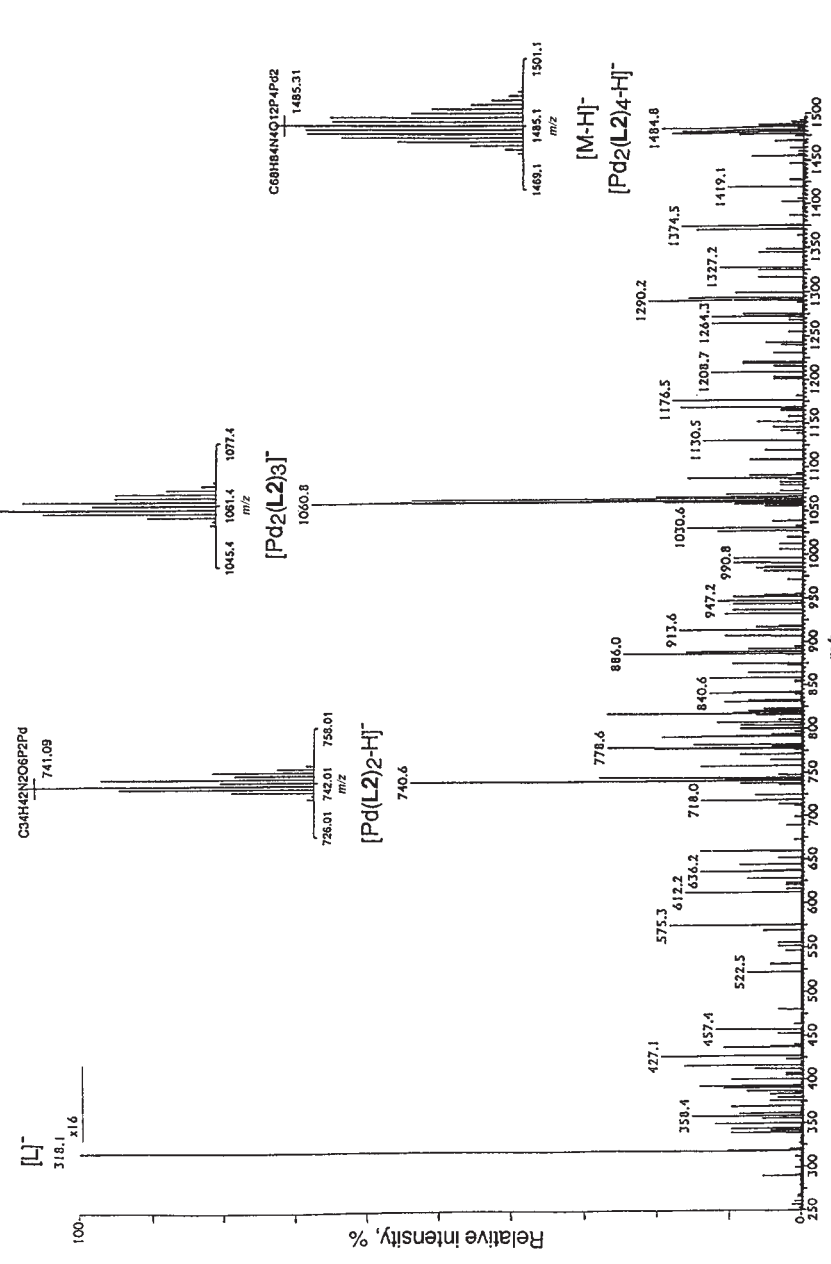

Figure 2. Negative-ion ESI mass spectrum of complex **2** (at a cone voltage of 30 V in methanol) and the theoretical isotopic mass distribution of the molecular and other Pd-containing fragment ions.

IR Spectra

The IR spectra of sodium salts as well as of palladium complexes are characterized by complex bands of medium to very strong intensity between 1240–1190 cm^{-1} for the antisymmetric and between 1085–995 cm^{-1} for the symmetric mode of the $\nu(PO_2^-)$ vibration. Variation in the position and complexity of these absorptions arises from their sensitivity to the nature of the metal ion.[15] In the latter frequency range, the ν(PO–C) absorption is superimposed upon that of the symmetric PO_2^- stretching vibration.[13,16] Changes in the spectra between sodium salts and palladium complexes may be noticed also between 1600 and 1500 cm^{-1} where the NH deformation modes, along with the benzene ring stretching vibrations, are found.

UV-VIS Spectra

The electronic absorption spectra of palladium complexes obtained in chloroform solution in the 260–600 nm region show a broad band at about 286 nm, and its position is close to that observed in free ligands. More intense absorption in the palladium complexes is predominantly due to contributions from different d-d transitions superimposed by the intraligand π–π^* transitions, while broadening of the absorption band on the low energy side could be ascribed to the metal-to-ligand charge-transfer transition. For the square-planar diamagnetic complexes, three spin allowed d–d transitions are expected, corresponding to transitions from the three lower d–levels to empty $d_{x^2-y^2}$ orbitals.[12,17]

NMR Spectra

The NMR spectra of palladium complexes are rather complex due to the existence of more isomeric species in dynamic equilibrium with different magnetic environments. This can be interpreted by the formation of a new chiral centre on the nitrogen atom caused by its coordination to palladium, as well as by the restricted rotation around the C–N linkage. It may be presumed that the arrangement of bonds around nitrogen approaches a tetrahedral configuration similar to that on the adjacent asymmetric benzyl carbon atom, as it was described for palladium complexes of dialkyl anilinobenzylphosphonates.[18] As a consequence, the ^1H NMR spectra of the complexes are characterized either by a signal broadening (in $CDCl_3$) or by an extensive signal splitting and their multiple overlap (in DMSO-d_6).

The existence of more isomeric species is clearly visible in the ^{31}P NMR spectrum of complex **2**, which exhibits a few signals between 23 and 35 ppm (Figure 3). The major isomer at 26.19 ppm, with abundance of *ca* 70%, could be ascribed to the less sterically hindered isomeric form. The fact that the ^{31}P NMR chemical shifts of the palladium complex do not differ much from

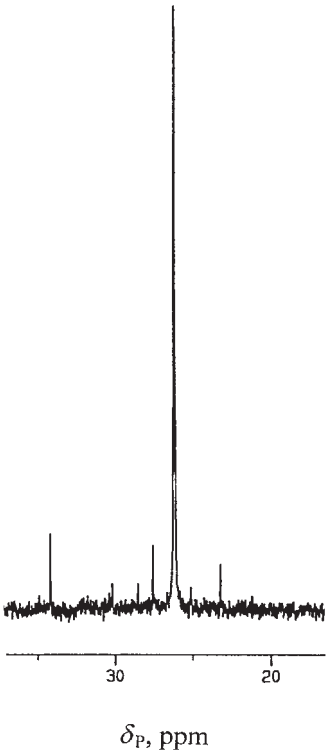

Figure 3. ^{31}P NMR spectrum of complex **2** in $CDCl_3$.

that observed for the sodium salt (23.24 ppm) supports the conclusion that coordination of phosphonate to metal ion is predominantly ionic and scarcely affects the phosphorus electron density.[19]

The results obtained by NMR spectral studies also indicate that the binuclear anilinobenzylphosphonate complexes are more stable than the mononuclear complexes derived from the corresponding benzeneazo-substituted phosphonate ligands. It was shown that both types of complexes retain their integrity in chloroform solution, while decomposition of the latter complexes could be noticed in DMSO.[13] This solvent with a strong complexing ability initiates dissociation of the mononuclear complex moiety by displacing the organophosphorus ligand, which is not observed in the case of binuclear complexes **1** and **2**.

Thermal Studies

Decomposition behaviour of the complexes was also investigated by thermogravimetric measurements accompanied by a infrared spectroscopic

TABLE I

TG and DTA data[a]

Compound	TG: Temp. range /°C	DTA: Dehalogenation and pyrolysis *T* /°C
Na**L1**	213–806	220 (exo), 240 (exo), 300 (exo), 395 (exo), 560 (exo), 625 (exo), 750 (exo)
1	190–816	170 (exo), 460 (exo), 540 (exo), 560 (exo), 605 (exo), 745 (exo)
	(134–829)	[265 (exo), 500 (exo)]
Na**L2**	198–812	155 (endo), 320 (exo), 400 (exo), 550 (exo), 600 (endo), 680 (endo)
2	174–819	161 (exo), 450 (exo), 512 (exo), 565 (exo), 680 (exo), 720 (exo)
	(130–825)	[245 (exo), 480 (exo), 510 (exo), 545 (exo), 565 (endo), 680 (exo)]

[a] Data for the PdL_2 complexes of monoethyl and monobutyl [4-α-(benzeneazo)-*N*-benzyl]phosphonates taken from Ref. 13 are given in parenthesis for comparison.

study. IR spectra were recorded every 50 °C and are compared with the corresponding spectra at room temperature. The results obtained from the TG and DTA curves are summarized in Table I and presented in Figure 4 for sodium salt Na**L1** and complex **1**. The TG curves of sodium salts show a sharp step between 200 and 350 °C with a rapid weight loss that corresponds to almost complete loss of organic matter. This decomposition process in DTA curves is visible as one (Na**L2**) or three (Na**L1**) exothermic effects in this temperature region. Further weight loss could be ascribed to partial sublimation of P_2O_5.[20] Thermal decomposition of the complexes occurs in two steps without formation of a stable intermediate. The first step, which covered approximately the range up to 300 °C, could be attributed to deesterification of the ligand. In the infrared spectra this is indicated by the loss of absorption bands arising from various modes of the Pd–OEt(Bu) groups around 1140 and 1025 cm^{-1} as well as of the alkyl C–C vibrations between 980–950 cm^{-1}. In the DTA curves, this process is visible as one exothermic peak at 170 and 161 °C, respectively. Decomposition of the complexes continues with a progressive weight loss, giving a mixture of Pd and P_2O_5, which was identified as the final pyrolytic residue by X-ray powder diffraction and infrared analyses. The intensity decrease of the phosphonate ester bands in the IR spectra is accompanied by the intensity increase of the P=O stretching band around 1235 cm^{-1}. Similar results were reported earlier for a number of palladium complexes of various aminophosphonic acid derivatives.[21,22]

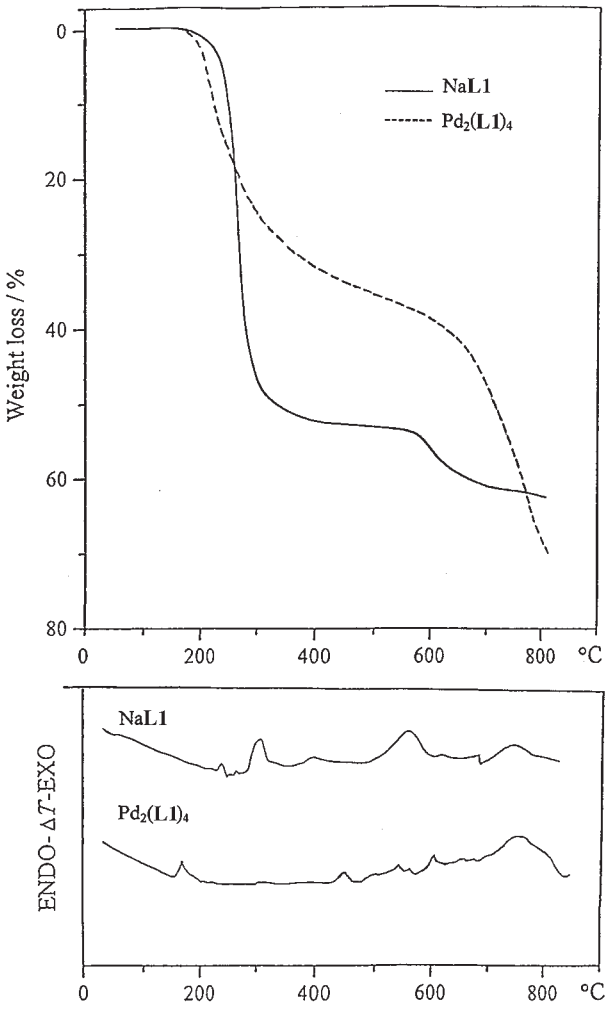

Figure 4. TG–DTA curves for Na**L1** (—) and complex **1** (----).

From the initial decomposition temperatures, which correspond to the beginning of the deesterification process, it may be seen that decomposition of the butyl derivatives started at lower temperatures compared to their ethyl analogues. It may be presumed that the stability of compounds decreases with the length of the alkyl ester group due to the increase of steric hindrance. When comparing the results of the binuclear five-membered [N,O] metallocyclic complexes **1** and **2** with those obtained for the corresponding mononuclear chelates of benzeneazoanilinophosphonates,[22] which are included in Table I for comparison, it may be concluded that dipalladium

complexes are more stable compounds. This behaviour is in agreement with the mass spectroscopic results as well as with the NMR studies. A lower stability of benzeneazoanilino phosphonate complexes could be ascribed partly to the relatively low basicity of the benzalaniline nitrogen in these compounds compared with that of the nitrogen in anilinobenzyl derivatives, caused by the interaction of its electron pair with the adjacent azobenzene π-system. In addition, there is the influence of steric factors since benzeneazoanilinophosphonates are much more bulky than anilinobenzylphosphonates. Steric effects also cause formation of mononuclear and not binuclear chelates of the azobenzene-substituted ligands. It may be concluded that both the geometric and steric requirements of the chelate ligand are very important in determining the final geometry and the stability of metallic species.

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SAŽETAK

Sinteza i karakterizacija metalocikličkih kompleksa paladija(II) s monoalkil (α-anilino-*N*-benzil)fosfonatima

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Opisana je sinteza te spektroskopska i termička svojstva peteročlanih [N,O] metalocikličkih kompleksa paladija(II) s monoetilnim (H**L1**) i monobutilnim (H**L2**) esterima (α-anilino-*N*-benzil)fosfonske kiseline. Binuklearni kompleksi Pd_2L_4 (L = **L1**, **L2**) dobiveni su reakcijom natrijevih soli monoalkilfosfonata s $PdCl_4^{2-}$ u vodi. Dva atoma paladija premošćena su sa četiri organofosforna liganda vezana preko anilinskog dušika i kisika deprotonirane fosfonske kiseline. Kompleksi su identificirani i karakterizirani elementnom analizom, te spektroskopskim (ESI-MS, IR, UV-VIS, ^{1}H i ^{31}P NMR) i termičkim (TG, DTA) istraživanjima. Svojstva kompleksa uspoređena su sa svojstvima metalocikličkih kompleksa paladija(II) s monoalkil 4-azobenzen-supstituiranim anilinobenzilfosfonatima.