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Synthesis and Structural Analysis of New Palladium(II) Thiosaccharinates with Triphenylphosphane or Diphosphanes

Susana H. Tarulli,[a] Oscar V. Quinzani,*[a] Sandra D. Mandolesi,[a] Jorge A. Guida,[b]
Gustavo A. Echeverría,[c] Oscar E. Piro,[c] and Eduardo E. Castellano[d]

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Abstract. A series of palladium(II) thiosaccharinates with triphenylphosphane (PPh_3), bis(diphenylphosphanyl)methane (dppm), and bis(diphenylphosphanyl)ethane (dppe) have been prepared and characterized. From mixtures of thiosaccharin, Htsac, and palladium(II) acetylacetonate, $Pd(acac)_2$, the palladium(II) thiosaccharinate, $Pd(tsac)_2$ (tsac: thiosaccharinate anion) (**1**) was prepared. The reaction of **1** with PPh_3, dppm, and dppe leads to the mononuclear species $Pd(tsac)_2(PPh_3)_2$·MeCN (**2**), $[Pd(tsac)_2(dppm)]$ (**3**), $Pd(tsac)_2(dppm)_2$ (**4**), and $[Pd(tsac)_2(dppe)]$·MeCN (**5**). Compounds **2**, **4**, and **5** have been prepared also by the reaction of $Pd(acac)_2$ with the corresponding phosphane and Htsac. All the new complexes have been characterized by chemical analysis, UV/Vis, IR, and Raman spectroscopy. Some of them have been also characterized by NMR spectroscopy. The crystalline structures of complexes **3**, and **5** have been studied by X-ray diffraction techniques. Complex **3** crystallizes in the monoclinic space group $P2_1/n$ with $a = 16.3537(2)$, $b = 13.3981(3)$, $c = 35.2277(7)$ Å, $\beta = 91.284(1)°$, and $Z = 8$ molecules per unit cell, and complex **5** in $P2_1/n$ with $a = 10.6445(8)$, $b = 26.412(3)$, $c = 15.781(2)$ Å, $\beta = 107.996(7)°$, and $Z = 4$. In compounds **3** and **5**, the palladium ions are in a distorted square planar environment. They are closely related, having two sulfur atoms of two thiosaccharinate anions, and two phosphorus atoms of one molecule of dppm or dppe, respectively, bonded to the Pd^{II} atom. The molecular structure of complex **3** is the first reported for a mononuclear Pd^{II}-dppm-thionate system.

Introduction

Metal-heterocyclic thioamides systems received much attention in the last decades because they are present in biological systems [1], they were also applied in the pharmaceutical industry [2]. Molecules containing nitrogen and sulfur donor atoms coordinated to platinum and gold, have been recognized for their *anti*-tumoral activity [3]. Moreover, a great number of Pd^{II} and Pt^{II} inorganic or organometallic complexes, specially with mono- and diphosphanes, were prepared and characterized as catalyst for a variety of oxidation, reduction or coupling reactions [4]. In the last years several works on Pd^{II} and Pt^{II} polynuclear complexes with a variety of anionic or neutral ligands were published and, in part, reviewed recently [5].

The heterocyclic thioamides (thiones) show thione-thiol tautomeric equilibria [6], a fact that makes them versatile chelating agents, especially for heavy metals [7]. Due to the large size of the sulfur atom and the proximity of the imine nitrogen atom, considerable bridging capabilities are also found for heterocyclic thionates, the deprotonated forms of thiones. η^1-S and η^1-N monodentating, η^2-S,N chelating, μ_2-S, μ_2-S,N, μ_3-S,N (η^2-S, η^1-N) and μ_4-S,N (η^3-S, η^1-N) bridging behaviors were observed, yielding from oligo- to polymeric species [7]. In contrast with the rich chemistry of thiones and thionates with metal cations as Cu^I, Ru^{II}, Ag^I, Pt^{II} or Hg^{II}, fewer palladium-thione compounds were studied and only the crystal structure of a small fraction of them were reported in the literature. Simple Pd^{II}-thionates (PdL_2) were generally prepared as almost insoluble compounds [8]. When L was benzothiazole-2-thionate, benzisothiazole-2-thionate, or pyridine-2-thionate, Pd_2L_4 molecular arrangements were observed, with the thionates acting as μ_2-S,N bridging ligands [8a, 8e, 8f]. Many ternary complexes prepared from the reaction of PdL_2 complexes or other Pd^{II} salts with mono or diphosphanes were also reported. In fact, *cis*- and *trans*-$[PdL_2(PR_3)_2]$, $[Pd(\eta^1\text{-}L)(\eta^2\text{-}L)(PR_3)]$, $[Pd(\eta^2\text{-}L)(PR_3)_2]X$, $[Pd(\eta^2\text{-}L)(PR_3)X]$, and $[Pd_2(\mu\text{-}L)_2(PR_3)_2X_2]$ (X: second anion) complexes with different types of thionates were synthesized [8c, 8d, 9]. Employing diphosphanes as co-ligands, several compounds with $[PdL_2(PP)]$ or

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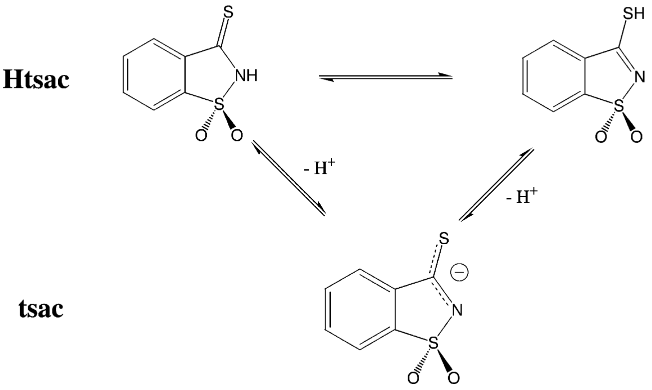
* Prof. Dr. O. V. Quinzani
Fax: +54-291-4595160
E-Mail: quinzani@criba.edu.ar
[a] INQUISUR, Departamento de Química
Universidad Nacional del Sur
Avda. Alem 1253
B8000CPB, Bahía Blanca, Argentina
[b] CEQUINOR, Facultad de Ciencias Exactas
Universidad Nacional de La Plata
C.C. 962
1900 La Plata, Argentina
and Departamento de Ciencias Básicas
Universidad Nacional de Luján
Rutas 5 y 7
Luján, Argentina
[c] Departamento de Física and Instituto IFLP
(Conicet, CCT La Plata)
Facultad de Ciencias Exactas, Universidad Nacional de La Plata
C.C. 67
1900 La Plata, Argentina
[d] Instituto de Física de São Carlos
Universidade de São Paulo
CP. 369
13560 São Carlos (SP), Brazil

[Pd(η^2-*L*)(PP)]*X* stoichiometries, with PP = dppm [3b, 8b, 9a, 10], dppe [9e, 10], dppp and dppb [8b, 10] were reported. Curiously, no crystal structure of the [PdL_2(dppm)]-type compound is currently found in the CCDC database and only two [PdL_2(dppe)]-type complexes are deposited there [9a, 10]. *Laguna* and co-workers prepared dinuclear Pd^{II} complexes with pyridine-2-thionate and dppm having the structures [Pd_2(μ_2-*S,N*-C_5H_4SN)(μ_2-κ^2-S-C_5H_4SN)(μ_2-dppm)(κ^1S-C_5H_4SN)$_2$] and [Pd_2(μ_2-*S,N*-C_5H_4SN)$_3$(μ_2-dppm)]Cl [11].

With the aim to further explore the coordination behavior of thiosaccharin, $C_6H_4S(O)_2NHC(S)$ (Htsac) (see Scheme 1), the thione form of saccharin, we studied new palladium thiosaccharinates. In the last years, we reported mono- and poly-nuclear structures of Ag^I, Pb^{II}, Cu^I, and Cd^{II} thiosaccharinates [12]. As was already reported, the thiosaccharinate anion can coordinate metal atoms through the endocyclic nitrogen and/or the hexocyclic sulfur atoms, therefore acting with a great variety of coordination modes [12d].



Scheme 1. Tautomeric and deprotonation equilibria of thiosaccharin.

In this work, we present the synthesis, X-ray structural analysis and spectroscopic characterization of two new palladium-thiosaccharinate complexes, namely bis(η^1-S-thiosaccharinato)-η^2-{bis(diphenylphosphanyl)methane)}palladium(II), [Pd(tsac)$_2$(dppm)], and bis(η^1-S-thiosaccharinato)-η^2-{bis(diphenylphosphanyl)ethane)}-palladium(II), [Pd(tsac)$_2$(dppe)]·MeCN. Palladium(II) thiosaccharinate, Pd(tsac)$_2$, and the two mononuclear species Pd(tsac)$_2$(PPh$_3$)$_2$·MeCN, and Pd(tsac)$_2$(dppm)$_2$ were also prepared and characterized.

Experimental Section

General Remarks

Palladium(II) acetylacetonate, triphenylphosphane, bis(diphenylphosphine)methane (dppm) and bis(diphenylphosphine)ethane (dppe), were purchased from Aldrich and used without further purification. Thiosaccharin (Htsac) in its α-form was prepared following the technique published by *Schibye* et al. [13] and characterized by melting point and IR spectroscopic analysis [14a]. Potassium thiosaccharinate, K(tsac), was prepared according to the procedure reported by *M. Penavic* et al. [14b]. Water was bi-destillated prior to use and the other solvents were of analytical reagent grade and dried by commonly used techniques [15]. The elemental composition analysis of C, N, H and S were performed with a Carlo Erba EA1108 instrument at INQUIMAE (FCEyN, UBA, Argentine). Conductivity measurements of dichloromethane (CH_2Cl_2) solutions of the compounds were performed with an OAKTON digital conductimeter calibrated against aqueous solutions of twice recrystallized KCl (744.7 ppm, 1413 μS).

Spectroscopic Measurements

The IR spectra of the substances as KBr pellets and Nujol mulls were recorded in the 4000 to 400 cm^{-1} range with a Nicolet Nexus FTIR spectrometer. The Raman spectra of the solids, run in the region between 3500 to 100 cm^{-1}, were obtained with a FRA 106 accessory mounted on a Bruker IFS 66 FTIR instrument, using the 1064 nm excitation line from an Nd-YAG laser. The UV/Vis spectra of the solutions and the KBr dispersed solids were registered using a Cecil 2021 spectrophotometer. The ^{1}H, ^{13}C and ^{31}P{^{1}H} NMR spectra of the compounds in [D$_6$]DMSO and $CDCl_3$ solutions, at 300 K, were recorded with multi-nuclear Bruker ARX-300 or Bruker AVANCE-300 instruments. The chemical shift data were measured employing the replacement methods and are given relative to external H_3PO_4 and TMS.

Synthesis

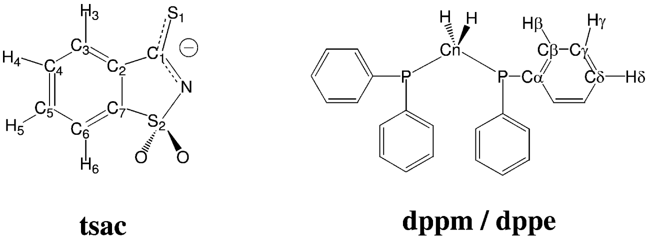
Palladium(II) Thiosaccharinate Pd(tsac)$_2$ (1): The yellowish-orange solid was obtained after dropwise addition of a solution of thiosaccharin (68.5 mg, 0.344 mmol) in acetonitrile (MeCN) (3 mL) to a solution of Pd(acac)$_2$ (52.4 mg, 0.172 mmol) in MeCN (5 mL), kept under constant stirring at room temperature, on dry air. The microcrystalline solid was collected by filtration, washed with small portions of MeCN and diethyl ether and afterwards dried on air. Yield: 66 mg (76 %). It shows almost the same spectroscopic features of the hydrated product obtained by *Vieytes* et al. [16]. All the procedures performed to obtain good crystals of the substance were unsuccessful. Analytical percent composition calculated for $C_{14}H_8N_2O_4PdS_4$: C 33.4; H 1.6; N 5.6 and S 25.5 %; Found: C 33.8; H 1.9; N 5.9, and S 25.9 %. Molar conductance ($\Omega^{-1}\cdot mol^{-1}\cdot cm^2$): 4 ($1.0 \times 10^{-5}$ M solutions in CH_2Cl_2). **IR** (KBr): $\tilde{\nu}$ = 1468s, 1422s, 1344s, 1241vs, 1182vs, 1131m, 1022s, 1011s, 803s, 598m, 555s cm^{-1}. **Raman** (pure solid) bands: 378m, 349s, 268m, 195w cm^{-1}. **UV/Vis** (CH_2Cl_2) λ_{max} (ε): 255 (28718), 294 (23821), 375 (sh) nm; (DMSO) λ_{max} (ε): 279 (36360), 339 (29920), 420 (sh) nm; (KBr disks) λ_{max} (ε): (240) (vs), 300 (w), 360 (w) nm.

Bis(thiosaccharinato)bis(triphenylphosphane)palladium(II) Monoacetonitrile Pd(tsac)$_2$(PPh$_3$)$_2$.CH$_3$CN (2): *Method 1*: PPh$_3$ (10.5 mg, 0.040 mmol) was added to an orange suspension of **1** (10.1 mg, 0.020 mmol) in MeCN (5 mL). After two hours of continuous stirring at 40 °C, the suspension became pale yellow. The solid was collected by filtration, washed with small portions of MeCN and diethyl ether and afterwards dried on air. Yield: 15 mg (70 %). All attempts to obtain single crystal samples of the substance suitable for X-ray diffraction analyses were unsuccessful, due to the extremely low solubility of the compound in common solvents. Analytical percent composition calculated for $C_{52}H_{41}N_3O_4P_2PdS_4$: C 58.5; H 3.9; N 3.9 and S 12.0 %; Found: C 58.4; H 3.2; N 4.0, and S 12.4 %. **IR** (KBr): $\tilde{\nu}$ = 2220vw, 1466s, 1435s, 1422m, 1316vs, 1229s, 1164vs, 1124m, 1096m, 999s, 800s, 693s, 588m, 512s cm^{-1}. **Raman** (pure solid) bands: 375m, 257s, 219m, 201m cm^{-1}. **UV/Vis** (KBr disks) λ_{max} (ε): 220 (vs), 276 (w), 318 (w), 365 (m) nm.

Method 2: Solid PPh$_3$ (31.6 mg, 0.120 mmol) was added to a MeCN solution (4 mL) of 18.3 mg (0.060 mmol) of Pd(acac)$_2$. The yellow solution was stirred for one hour at 40 °C. After that, a MeCN solution

(3 mL) containing thiosaccharin (23.9 mg, 0.120 mmol) was dropped on and a clear yellow solid immediately appeared. The suspension was stirred also for one hour and then filtered off. The solid was washed with small portions of MeCN and diethyl ether, and then air dried. Yield 30 mg (47 %).

Bis(thiosaccharinato){bis(diphenylphosphanyl)methane}palladium(II) Pd(tsac)$_2$(dppm) (3): A solution of dppm (11.5 mg, 0.030 mmol) in MeCN (3 mL) was added to a suspension of **1** (15.1 mg, 0.030 mmol) in MeCN (5 mL) at 30 °C with continuous stirring. After one hour, the suspension became a clear yellow solution. The solution was warmed and evaporated until it reached a third of its original volume. It was kept at 10 °C for one day after which pale yellow crystals, suitable for X-ray diffraction analysis, formed. Yield 14.2 mg (53 %). Analytical percent composition calculated for $C_{39}H_{30}N_2O_4P_2PdS_4$: C 52.8; H 3.4; N 3.2 and S 14.5 %; Found: C 52.8; H 3.7; N 3.2, and S 14.6 %. Molar conductance ($\Omega^{-1}\cdot mol^{-1}\cdot cm^2$): 2 ($6.0 \times 10^{-4}$ M solutions in CH_2Cl_2). **IR** (KBr): $\tilde{\nu}$ = 1460s, 1436s, 1407m, 1308vs, 1229s, 1153vs, 1123s, 1105m, 1000s, 809s, 738s, 689m, 588m cm^{-1}. **Raman** (pure solid) bands: 370s, 257s, 228m, 168s cm^{-1}. **UV/Vis** (CH_2Cl_2) λ_{max} (ε): 265 (35000), 350 (6200) nm; (KBr disks) λ_{max} (ε): (200) (vs), 230 (sh), 295 (w), 360 (w) nm. **^{1}H NMR** ($CDCl_3$): δ = 7.93–7.77 (m, 10 H, H6 tsac and Hβ dppm); 7.70–7.62 (m, 2 H, H3 tsac); 7.58–7.49 (m, 4 H, H4/H5 tsac); 7.49–7.35 (m, 12 H, Cδ/Cγ dppm); 4.22 (t, 2 H, CH$_2$, J^2 / ^{31}P: 9.9 Hz). **^{13}C NMR** ($CDCl_3$): tsac: δ = 184.53 (C1); 138.19 (C7); 134.21 (C2); 132.63 (C5); 131.65 (C4); 125.04 (C6); 120.26 (C3); dppm: δ = 133.44 (d, Cβ, ^{3}J(^{13}C, ^{31}P), 6.0 Hz); 133.36 (d, Cβ', ^{2}J(^{13}C, ^{31}P), 6.0 Hz); 132.34 (Cδ); 129.44 (d, Cγ, ^{3}J(^{13}C, ^{31}P),6.0 Hz); 129.36 (d, Cγ', ^{3}J(^{13}C, ^{31}P),6.0 Hz); 127.01 (d, Cα, ^{1}J(^{13}C, ^{31}P),24.9 Hz); 126.73 (d, Cα', ^{1}J(^{13}C, ^{31}P), 25.0 Hz); 42.60 (t, CH$_2$, ^{1}J(^{13}C, ^{31}P), 24.8 Hz). **^{31}P{^{1}H} NMR** ($CDCl_3$): δ = 10.42 (s). The atom numbering for the NMR spectroscopic data is shown in Scheme 2.



Scheme 2. Atoms numbering for tsac, dppm and dppe molecules.

Bis(thiosaccharinato)bis{bis(diphenylphosphanyl)methane}-palladium(II) Pd(tsac)$_2$(dppm)$_2$ (4): *Method 1*: A solution of dppm (23.1 mg, 0.060 mmol) in MeCN (2 mL) was added to a suspension of **1** (15.1 mg, 0.030 mmol) in MeCN (2 mL). The mixture was stirred for two hours at 40 °C. The initial bright yellow suspension gradually faded and the residual solid was filtered off, washed with small portions of MeCN and diethyl ether, and afterwards dried on air. Yield 17.3 mg (45 %). Analytical percent composition calculated for $C_{64}H_{52}N_2O_4P_4PdS_4$: C 60.5; H 4.1; N 2.2 and S 10.1 %; Found: C 59.7; H 4.0; N 2.4, and S 10.0 %. Molar conductance ($\Omega^{-1}\cdot mol^{-1}\cdot cm^2$): 5 ($1.0 \times 10^{-3}$ M solutions in CH_2Cl_2). **IR** (KBr): $\tilde{\nu}$ = 1464s, 1434s, 1421m, 1315s, 1229s, 1163vs, 1123m, 1099m, 1000s, 801s, 737m, 695s, 588m, 555s cm^{-1}. **Raman** (pure solid) bands: 371m, 255m, 166m cm^{-1}. **UV/Vis** (CH_2Cl_2) λ_{max} (ε): 255 (70000), 285 (36000), 325 (6000) nm; (KBr disks) λ_{max} (ε): (200) (vs), 290 (w), 356 (w) nm.

Method 2: A solution of dppm (30.8 mg, 0.080 mmol) in MeCN (2 mL) was added to a solution of Pd(acac)$_2$ (12.2 mg, 0.040 mmol) in MeCN (8 mL). The yellow solution was stirred for one hour at 50 °C. Afterwards, a solution of thiosaccharin (15.9 mg, 0.080 mmol) in MeCN (3 mL) was added. After about twenty minutes a yellow solid appears that was filtered off, washed with small portions of MeCN and diethyl ether, and afterwards dried on air. Yield 11 mg (22 %).

Bis(thiosaccharinato){bis(diphenylphosphanyl)ethane}palladium(II) Monoacetonitrile Pd(tsac)$_2$(dppe)·MeCN (5): *Method 1*: Dppe (15.9 mg, 0.040 mmol) was added to a suspension containing Pd(tsac)$_2$ (20.1 mg, 0.040 mmol) in MeCN (7 mL). The initially bright yellow reaction mixture was stirred for three hours at room temperature, until its color gradually turned to pale yellow. The solid was filtered, washed with small portions of MeCN and diethyl ether and afterwards dried on air. Yield 29.1 mg (81 %). Analytical percent composition calculated for $C_{42}H_{35}N_3O_4P_2PdS_4$: C 53.5; H 3.7; N 4.5 and S 13.6 %; Found: C 53.5; H 4.0; N 4.1; and S 14.0 %. Molar conductance (Ω^{-1} mol^{-1} cm^{-1}): 2 (1.0×10^{-3} M solutions in CH_2Cl_2). **IR** (KBr): $\tilde{\nu}$ = 1463s, 1437s, 1416s, 1309vs, 1232s, 1155vs, 1123s, 1106m, 1002s, 887m, 807s, 754m, 691s, 555s, 535s cm^{-1}. **Raman** (pure solid) bands: 368m, 257s, 233m, 158s cm^{-1}. **UV/Vis** (CH_2Cl_2) λ_{max} (ε): 265 (41200), 334 (6240) nm; (KBr disks) λ_{max} (ε): (210) (vs), 286 (w), 375 (w) nm. **^{1}H NMR** ([D$_6$]DMSO): δ = 8.25–8.09 (m, 8 H, Hβ dppe); 8.08–8.01 (m, 2 H, H6 tsac); 7.97–7.88 (m, 2 H, H3 tsac); 7.88–7.79 (m, 4 H, H4/H5 tsac); 7.79–7.62 (m, 12 H, Cγ/Cδ dppe); 2.92 (m, 4 H, CH$_2$). **^{13}C NMR** ([D$_6$]DMSO): tsac: δ = 184.92 (C1); 137.74 (C7); 133.54 (C5); 132.73 (C4); 124.66 (C6); 120.57 (C3); dppe: δ = 133.79(d, Cβ, ^{2}J(^{13}C, ^{31}P), 12.3 Hz) 132.45 (Cδ); 129.28 (d, Cγ, ^{3}J(^{13}C, ^{31}P), 11.7 Hz); 127.34 (d, Cα, ^{1}J(^{13}C, ^{31}P), 41.9 Hz); 27.76 (dd, CH$_2$, ^{2}J(^{13}C, ^{31}P), 12.9 Hz); ^{1}J(^{13}C, ^{31}P), 32.8 Hz). **^{31}P{^{1}H} NMR** ([D$_6$]DMSO): δ = 120.44 (s).

Upon slow evaporation of saturated solutions of the complex in acetonitrile, well formed yellow crystals of compound **5** were collected. These crystals were employed in the structural X-ray diffraction study reported herewith.

Method 2: To a solution containing Pd(acac)$_2$ (12,2 mg, 0.040 mmol) and dppe (32.0 mg, 0.080 mmol) in MeCN (8 mL), another MeCN solution (2 mL) containing thiosaccharin (16.0 mg, 0.080 mmol) was added under constant stirring at 50 °C. The small amount of a pale yellow solid formed was filtered off and the clear solution was slowly evaporated, at room temperature. After three days, a mixture of yellow and small orange crystals appeared. The yellow solid correspond to compound **5** and the orange solid seemed to be a Pd^I complex similar to the dinuclear Pd$_2$(dppm)$_2$(tsac)$_2$ compound (**6**) (see below) [17].

X-ray Diffraction Data

Crystal data, data collection procedure, structure determination methods and refinement results for complexes **3** and **5** are summarized in Table 1 [18–24].

The hydrogen atoms were positioned stereo-chemically and refined with the riding model. The methyl hydrogen atoms of the crystallization acetonitrile molecule in **5** were optimized by treating them as a rigid groups that were allowed to rotate around the corresponding C–C bond. ORTEP [25] molecular drawings of the complexes are shown in Figure 2 and Figure 3. CIF files containing details of the crystal structures reported in the paper have been deposited with the Cambridge Structural Data Base and are available free of charge upon request from The Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. (Fax: +44-1233-336033; E-Mail: deposit@ccdc.cam.ac.uk; WEB: http://www.csdc.cam.ac.uk), reference numbers CCDC-718963 (**3**), and CCDC-718964 (**5**).

Table 1. Crystal data and refinement results for [Pd(tsac)$_2$(dppm)] (**3**), and [Pd(tsac)$_2$(dppe)]·MeCN (**5**).

	3	**5**
Empirical formula	$C_{39}H_{30}N_2O_4P_2PdS_4$	$C_{42}H_{35}N_3O_4P_2PdS_4$
Formula weight	887.23	942.31
Temperature /K	150(2)	293(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions[a)]		
a /Å	16.3537(2)	10.6445(8)
b /Å	13.3981(3)	26.412(3)
c /Å	35. 2277(7)	15.781(2)
β /°	91.284(1)	107.996(7)
Volume /Å^3	7716,8(2)	4219.7(8)
Z, calculated density /Mg·m^{-3}	8, 1.527	4, 1.483
Absorption coefficient /mm^{-1}	0.824	6.481
F(000)	3600	1920
Crystal size /mm	0.12 × 0.03 × 0.02	0.24 × 0.24 × 0.10
Crystal color / shape	yellow / plate	yellow / plate
Diffractometer / scan	KappaCCD / φ and ω	Enraf–Nonius CAD4 / ω–2J
Radiation	Mo-K_α, λ = 0.71073 Å	Cu-K_α, λ = 1.54184 Å
ζ range data collection /°	3.04 to 26.00	3.35 to 68.03
Index ranges	$-20 \le h \le 12$, $-16 \le k \le 16$, $-43 \le l \le 43$	$-12 \le h \le 12$, $-1 \le k \le 30$, $-18 \le l \le 0$
Completeness /%	99.7 (to J = 26.00°)	98.0 (to J = 68.03°)
Observed reflections [$I > 2\sigma(I)$]	10394	6129
Data collection	COLLECT [18]	EXPRESS [19]
Data reduction[b)]	DENZO-SCALEPACK [20]	XCAD4 [21]
Absorption correction	Numerical [22]	
Structure solution[c)]	SHELXS-97 [23]	
Refinement[d)]	SHELXL-97 [24]	
Refinement method	Full matrix least-squares on F^2	
Weights /w	$[\sigma^2(F_o^2)+(0.051P)^2]^{-1}$ $P = [\mathrm{Max}(F_o^2,0)+2F_c^2]/3$	$[\sigma^2(F_o^2)+(0.069P)^2+4.79P]^{-1}$ $P = [\mathrm{Max}(F_o^2,0)+2F_c^2]/3$
Goodness-of-fit on F^2	1.014	1.051
Reflections collected/unique	57765/15144	8158/7522
R(int)	0.0792	0.0452
Data / restraints / parameters	15144 / 0 / 937	7522 / 0 / 508
R_1(obs,), R_1(all)[e)]	0.0452, 0.0949	0.0443, 0.0571
wR_2(obs,), wR_2(all)[e)]	0.0795, 0.1040	0.1187, 0.1324
Largest peak and hole /e.A^{-3}	0.863 and –0.814	0.651 and –1.443

a) Least-squares refinement of the angular settings for 57765 reflections in the 3.04<J<26.00° range for **3** and 24 reflections in the 16.48 < J < 34.36° range for **5**. b) Corrections by Lorentz and polarization effects. c) Neutral scattering factors and anomalous dispersion corrections. d) Structure solved by direct and Fourier methods. The final molecular model obtained by anisotropic full-matrix least-squares refinement of the non-hydrogen atoms. e) R indices defined as: $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Supporting Information: Listings of fractional atomic coordinates and equivalent isotropic displacement parameters (Tables S7–8), full intramolecular bond lengths and angles (Tables S9–10), atomic anisotropic displacement parameters (Tables S11–12) and hydrogen atoms positions (Tables S13–14), along with tables of full IR-Raman data for complexes **1** to **5** (Table S15) can be obtained from the authors upon request.

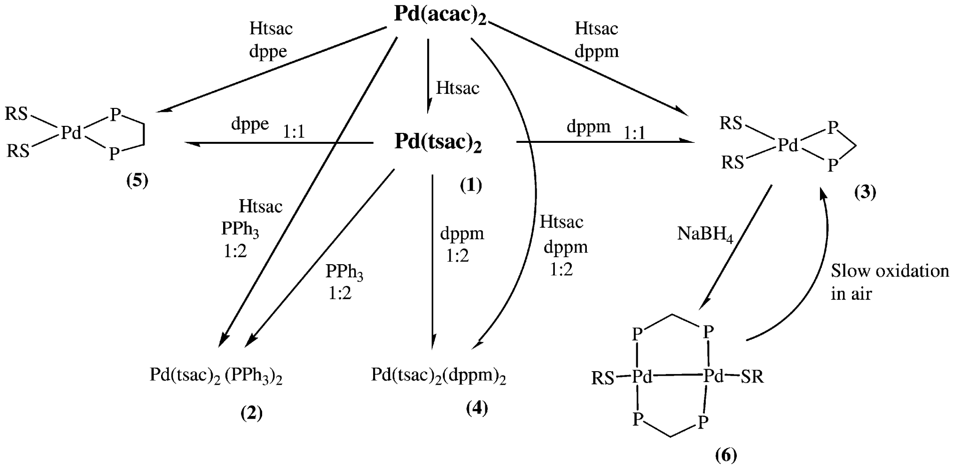
Results and Discussion

Chemistry of Palladium(II) and Palladium(I) Thiosaccharinates

As it is well-known for other heterocyclic thiones, thiosaccharin shows a tautomeric equilibrium in solution (see Scheme 1). It is present in its thiol form in dimethylsulfoxide solutions and in the thione form in non-coordinating solvents, as was observed by NMR spectroscopy [26]. In the solid state it shows only the thione form [14a]. Its thiolate (thionate) form can act as a good coordinating agent for soft metals, hence giving rise to mononuclear and poly-nuclear structures with or without the presence of other ligands.

The yellowish-orange little soluble palladium(II) thiosaccharinate (**1**) was obtained by the direct reaction of palladium(II) salts (nitrate or acetylacetonate) with thiosaccharin in water, light alcohols or MeCN. When PPh_3 is added to suspensions of **1** in MeCN, a very insoluble ternary palladium(II) thiosaccharinate (**2**) was obtained (Scheme 3).

When 1:1 molar relations between **1** and diphosphanes (dppm or dppe) are mixed in MeCN, pure solids are obtained (**3 and 5**). The single-crystal X-ray diffraction analysis of both compounds showed the presence of mononuclear complexes, with S_2P_2 square coordination spheres around the metal. Complexes **3** and **5** are insoluble in water, moderately soluble in MeCN or $CHCl_3$, and soluble in DMSO. They are indefinitely air and light stable. Using a 1:2 molar relationship between **1** and dppm, in MeCN, a new solid compound (**4**) is obtained.



RS = thiosaccharinate anion (tsac)

Scheme 3. Synthesis of the Pd^{II}-thiosaccharinate complexes.

The spectroscopic data of complex **4** show that the Pd^{II} atoms are surrounded by two sulfur atoms of thiosaccharinate anions and two phosphorus atoms of two different monocoordinated dppm molecules.

Reducing a suspension of [Pd(tsac)$_2$(dppm)] in MeCN with NaBH$_4$, the orange dipalladium(I) complex [Pd$_2$(dppm)$_2$-(tsac)$_2$] (**6**) is obtained. Its crystal X-ray diffraction analysis showed a side-by-side "Pd$_2$(μ-dppm)$_2$" framework with the thiosaccharinate ligands coordinated to the metal centers through their exocyclic sulfur atoms [17]. Complex **6** is indefinitely stable to moisture in its solid form. In solution, and in the presence of oxygen, the yellow complex **3** slowly forms and can be recovered in crystalline form upon evaporation.

Structural and Spectroscopic Analysis of Palladium(II) Thiosaccharinates

Spectroscopic Analysis of Pd(tsac)$_2$ (1)

As discussed in our previous reports the most detachable vibrational bands useful for structural analysis, correspond to the vibrations of the five membered isothiazol and the thiocarbon-

Table 2. Selected infrared (IR) and Raman (R) bands (in cm^{-1}) for Pd(tsac)$_2$ (**1**), Pd(tsac)$_2$(PPh$_3$)$_2$·MeCN (**2**), [Pd(tsac)$_2$(dppm)] (**3**), Pd(tsac)$_2$(dppm)$_2$ (**4**), and [Pd(tsac)$_2$(dppe)]·MeCN (**5**)$^{a)}$.

1		**2**		**3**		**4**		**5**		Assignment
IR$^{b)}$	R	IR	R	IR	R	IR	R	IR	R	
		2220vw						2245vw		ν(CN) MeCN
		1435s		1436s	1434w	1434s		1437s	1440w	ν(CC) PPh$_n$
1422s	1392s	1422m	1422s	1408m	1408s	1421m	1421s	1416s	1416s	ν(CN) ν(CC)
1344s		1316vs		1308vs		1315s	1312vw	1309s		ν_{as}(SO$_2$)
1241vs	1239vs	1229s	1234vs	1229s	1229vs	1229s	1230vs	1232s	1233vs	ν(φC)δ = (CCC)
1182vs	1179s	1163vs	1154s	1153vs	1153s	1163vs	1157m	1155vs	1159s	ν_s(SO$_2$)
1129s		1124m		1123s		1123m	1128vw	1123s		ν(φS) ν(CS)
		1096m	1093s	1105m	1106s	1099m	1099m	1106m	1104s	δ(CH) PPh$_n$
1022/1011s	1015s	999 s		1000vs		1000s		1002s		ν(CS)δ = (CNS)
			999vs		998vs		998vs		999vs	ν(CC) PPh$_n$
805s		800s		809s		801s		808s		ν(NS)
		693 s	699m	689m	698m	695s	696m	691s	695m	ν_{as}(PPh$_n$)
598 s	596m	588m	592w	588m	588w	588m	589vw	589m		γ(CCC) δ(SO$_2$)
	378m		375m		370 s		371m		368m	γ(isoindol)
	349s		331w		323m		333w		324m	ν(PdS) ν(NS)
	268m									ν(PdN)
			257 s		257s		255m		257s	δs(PC$_n$)
			219m		228m		217w		233m	vas(PPdP)
										δ(isoindol)
			166m		168m		166m		179m	vs(PPdP)

a) tsac = thiosaccarinate anion. b) vs: very strong, s: strong, m: medium, w: weak, vw: very weak, br: broad.

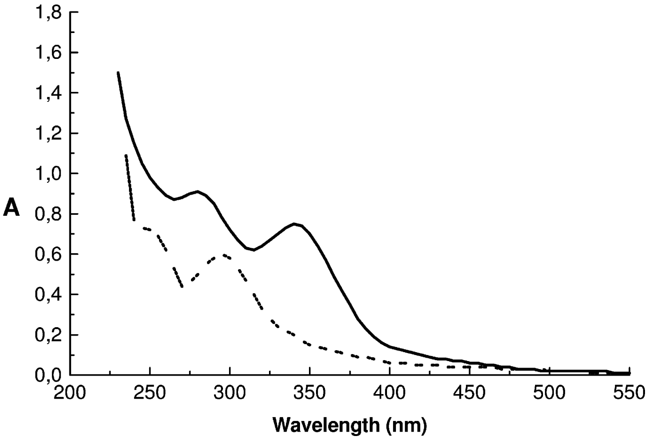


Figure 1. Electronic spectra of 2.0×10^{-5} m solutions of $Pd(tsac)_2$ (**1**): ——— in DMSO; - - - - in CH_2Cl_2.

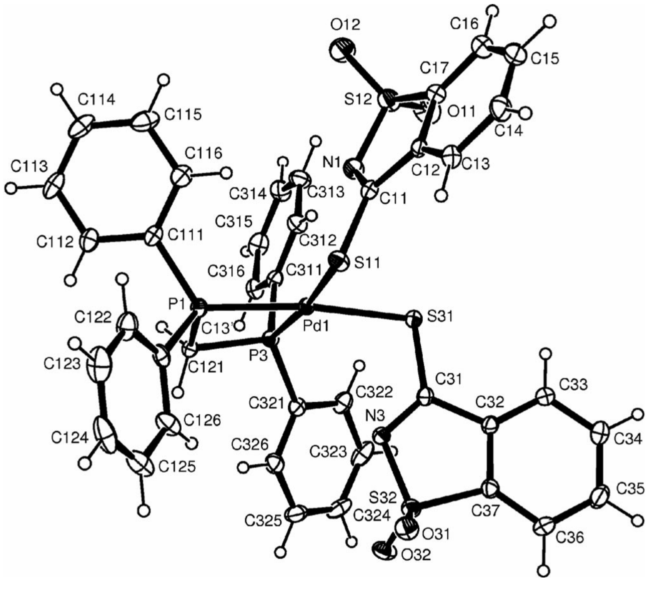


Figure 2. Molecular plot of $[Pd(tsac)_2(dppm)]$ (**3**) showing the labeling of the non-hydrogen atoms and their displacement ellipsoids at the 30 % probability level.

ilic groups [12]. These characteristic bands are assigned in Table 2 considering our previous works and also published theoretical vibration analysis of other authors [27]. For the "free" non-coordinating anion in the ionic bis(tryphenylphosphine)iminium thiosaccharinate, PNP(tsac), the bands owing to the stretching vibrations of the C–N and C–S_{exo} bonds are located at 1365 and 1010 cm^{-1}, respectively [26].

Three observations on the vibrational spectroscopic data of the solid complex **1** indicate that the tsac anions are acting as S,N-bridges or S,N-chelates: a) the difference in wavenumbers between the IR and Raman bands assignable to the stretching motions of the C–N bonds [1422 (IR) and 1392 (R) cm^{-1}] and the C–S_{exo} bonds [1022/1011 (IR) and 1015 (R) cm^{-1}], b) the relatively high energy of the stretching vibrations of the C–S_{exo} bonds, and c) the existence of low energy Raman dispersions assignable to stretching motions of Pd–S and Pd–N bonds (349 and 268 cm^{-1}, respectively) [28].

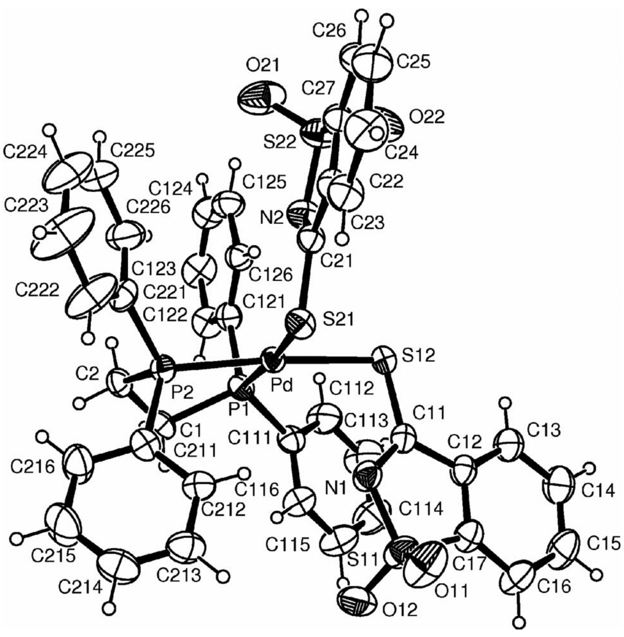


Figure 3. Molecular plot of $[Pd(tsac)_2(dppe)]\cdot MeCN$ (**5**).

There are three possible molecular structures for the binary compound **1**: a) a square planar mononuclear $Pd(tsac)_2$ form, with two S,N-chelating tsac ligands, b) a dinuclear $Pd_2(tsac)_4$ form, with four S,N-bridging tsac ligands between the two Pd^{II} atoms, or c) a polynuclear $Pd_n(tsac)_n$ form, with the tsac ligands acting as μ_3-S,N bridges between the Pd^{II} atoms. The first structure is the less possible because it needs two strained four membered rings formed by S,N-chelating heterocyclic thionates [9e]. As was already pointed out, binary Pd^{II} thionates with dinuclear arrangements are known [8]. For the complex $[Pd(py2S)_2]_2\cdot 2CHCl_3$ (py2S = pyridine-2-thionate), *K. Umakoshi* et al. reported the existence of an inversion center with a short Pd–Pd distance of 2.622 Å and PdS_2N_2 *cis*-square arrangements for the two Pd^{II} atoms [8f]. They reported also a medium intensity band in the UV/Vis spectra in solution, centered at 430 nm, indicative of the existence of a "Pd–Pd" bond in the complex [8f]. In the electronic spectra of complex **1** in the solid state and in diluted CH_2Cl_2 solutions, no such bands were observed (Figure 1) and the type b) molecular arrangement is discarded. So, some kind of polynuclear molecular structure is expected for the palladium(II)-thiosaccharinate complex. The electronic spectra of **1** show differences between the CH_2Cl_2 and DMSO solutions (Figure 1). In the former solvent a low energy band at 294 nm appeared, which can be assigned to the $\pi\rightarrow\pi^*$ transition of the C=S bond in the tsac anions [12f, 29]. The solid substance dispersed in KBr shows a similar low energy band at 300 nm. In the spectra of **1** in DMSO, this band is shifted to 339 nm, too much to be assigned to a solvent effect. Probably a dissociation process occurs and mononuclear species of the type $Pd(tsac)_2(DMSO)_2$ appear [12f]. This behavior agrees with the NMR spectroscopic data in $[D_6]$DMSO. The thiocarbonilic carbon atoms

(C1) show a unique ^{13}C NMR signal (189 ppm) low-field shifted against to Htsac (161 ppm) and slightly shifted up-field against the free thiosaccharinate anion (191 ppm) [16]. In weak coordinating solvents like CH_2Cl_2, the poly-nuclear structure of the solid complex **1** could be retained.

*Crystal Structure of [Pd(tsac)$_2$(dppm)] (**3**)*

There are two closely related complexes per asymmetric unit. Figure 2 shows a drawing of one of these molecules. Bond lengths and angles around the palladium(II) ions are listed in Table 3.

Table 3. Selected bond lengths /Å and angles /° around Pd^{II} ion in [Pd(tsac)$_2$(dppm)] (**3**) and [Pd(tsac)$_2$(dppe)]·MeCN (**5**) complexes.

[Pd(tsac)$_2$(dppm)]		[Pd(tsac)$_2$(dppe)]	
Bond lengths			
Pd(1)–P(1)	2.2696(10)	Pd–P(1)	2.2510(14)
Pd(1)–P(3)	2.2479(10)	Pd–P(2)	2.2566(14)
Pd(2)–P(2)	2.2383(10)		
Pd(2)–P(4)	2.2762(10)		
Pd(1)–S(11)	2.4017(10)	Pd–S(11)	2.3806(14)
Pd(1)–S(31)	2.3905(10)	Pd–S(21)	2.3834(14)
Pd(2)–S(21)	2.3702(10)		
Pd(2)–S(41)	2.4012(10)		
Angles			
P(1)–Pd(1)–P(3)	73.23(4)	P(1)–Pd–P(2)	84.86(5)
P(1)-Pd(19-S(11)	102.03(4)	P(1)–Pd–S(11)	89.59(5)
P(3)–Pd(1)–S(11)	174.13(4)	P(2)–Pd–S(11)	173.49(5)
P(1)–Pd(1)–S(31)	166.79(4)	P(1)–Pd–S(21)	175.18(5)
P(3)–Pd(1)–S(31)	93.98(4)	P(2)–Pd–S(21)	90.97(5)
S(11)–Pd(1)–S(31)	90.93(4)	S(11)–Pd–S(21)	94.71(5)
P(2)–Pd(2)–P(4)	72.84(4)		
P(2)–Pd(2)–S(21)	91.65(4)		
P(4)–Pd(2)–S(21)	162.60(4)		
P(2)–Pd(2)–S(41)	174.53(4)		
P(4)–Pd(2)–S(41)	102.75(4)		
S(21)–Pd(2)–S(41)	93.15(4)		

In both complexes, the Pd^{II} atom is in a distorted square environment, *cis*-coordinated to a dppm molecule acting as a bidentate ligand through its phosphorus atoms [Pd1–P bond lengths of 2.248(1) and 2.260(1) Å and bite P1–Pd1–P3 angle of 73.24(4)°; Pd2–P bond lengths of 2.238(1) and 2.276(1) Å and ∠(P2–Pd2–P4) = 72.84(4)°] and to the exocyclic sulfur atom of two thiosaccharinate anions [Pd1–S distances of 2.391(1) and 2.401(1) Å and ∠(S11–Pd1–S31) = 90.92(3)°; Pd2–S lengths of 2.371(1) and 2.401(1) Å and ∠(S21–Pd2–S41) = 93.15(4)°]. Trans P–Pd–S angles are 166.80(4) and 174.13(4)° for complex **1** and 162.60(4) and 174.58(4)° for complex **2**.

As far as we know, complex **3** is the first Pd^{II}-thionate structure with a chelating dppm molecule reported. Other Pd^{II}-thionate-dppm mixtures yield dinuclear complexes with the diphosphane acting as bridges (see as an example the work of *A. Mendia* et al. [11]). *G. L. Palenik* et al. prepared the mononuclear complex [Pd(dppm)(SCN)$_2$], which has also a square planar metal environment built by two phosphorus atoms of a chelating dppm molecule and two sulfur atoms of two η^1-S-thiocyanate ligands [30]. The average Pd–P (2.258 Å) and Pd–S (2.391 Å) distances of complex **3** are a little shorter and longer, respectively, than in [Pd(dppm)(SCN)$_2$] (2.273 and 2.364 Å, respectively), maybe because of steric effects of the bulky tsac anions. The structural parameters of the dppm ligand are almost the same as those observed in other diphosphane complexes [11, 30].

*Crystal Structure of [Pd(tsac)$_2$(dppe)]·MeCN (**5**)*

Figure 3 shows a molecular drawing of the complex. Bond lengths and angles around the palladium atom are included in Table 3.

The conformation of Pd(tsac)$_2$(dppe) complex is closely related to Pd(tsac)$_2$(dppm) (see Figure 1 and Figure 2). The Pd^{II} ion is in a less distorted environment [Pd–P bond lengths of 2.251(1) and 2.256(1) Å and bite P–Pd–P angle of 84.90(4)°; Pd–S bond lengths of 2.380(1) and 2.383(1) Å and ∠(S–Pd–S) = 94.72(4)°], as expected for the more flexible chelating P–CH_2–CH_2–P group of dppe ligand as compared with the P–CH_2–P group of dppm.

Several molecular structures of square planar [Pd(dppe)T$_2$] (T: thiolate anion) compounds were reported in literature [31]. *Lobana* et al. reported the crystalline structures of the complexes [Pd(pym2S)$_2$(dppe)] (pym2S = 2-mercaptopyrimidine) and [Pd(py2S)$_2$(dppe)], as part of the study of mononuclear Pd^{II} thionates with several diphosphanes: dppm, dppe, dppp, dppmS and dppmSe ligands [9a, 10]. As far as we know, those complexes are the only two mononuclear Pd^{II}-thionate-dppe complexes previously reported. The averaged Pd–P (2.254 Å) and Pd–S (2.382 Å) distances of complex **5** are slightly different from corresponding values reported for [Pd(pym2S)$_2$(dppe)] (2.2770 and 2.3808 Å, respectively) [9a], and [Pd(py2S)$_2$(dppe)] (2.280 and 2.358 Å, respectively) [10], hence suggesting the presence of steric hindrance between the tsac ligands. This effect is also observed in the value of the S–Pd–S angle between thionates [94.71(5)°], greater than in the [Pd(pym2S)$_2$(dppe)] and [Pd(py2S)$_2$(dppe)] complexes (89.13 and 83.90°, respectively). The structural parameters of the dppe ligand are almost the same in the three complexes.

The similar complex [Pd(dppe)(SCN)(NCS)] was prepared and its molecular structure was reported by *Palenik* et al. [30]. The most important difference in comparison to complex **5** is the composition of the square-planar coordination sphere of the Pd^{II} atoms in both complexes: a P_2S_2 environment in complex **5** and a P_2SN sphere in the *Palenik* et al. compound. The latter shows longer Pd–P distances [2.252(2) and 2.264(2) Å] and shorter Pd–S bond length [2.252(2) Å] than complex **5**. The conformation and structural parameters of the dppe ligands in both complexes are almost the same.

*Spectroscopic Analysis of the Complexes [Pd(tsac)$_2$(PPh$_3$)$_2$] (**2**), [Pd(tsac)$_2$(dppm)] (**3**), [Pd(tsac)$_2$(dppm)$_2$] (**4**) and [Pd(tsac)$_2$(dppe)] (**5**)*

For the ternary complexes **2** to **5** the vibration bands assigned to the stretching motions of C–N and C–S$_{exo}$ bonds (Table 2) confirm the presence of the tightly bonded thiosaccharinate ligands [12, 32]. The positions of the two bands are slightly different to the values observed for other coordination forms of the thiosaccharinate anion, like 1419/1003 cm^{-1} for η^2-N,S [12h] or 1411/997 cm^{-1} for μ_2-S [12f]. The Raman bands of medium intensity appearing at ca. 320 and 230 cm^{-1} were assigned to stretching vibrations of the Pd–S and Pd–P bonds, according to the theoretical vibrational calculations performed for the complex $[Pd_2(dppm)_2(tsac)_2]$ [17]. The stretching vibrations of the SO_2 groups, principally the *anti*-symmetric mode, show that the oxygen atoms are not involved in hydrogen bridges. The assignments of the phosphine internal movements were made according to vibrational studies of other authors [33]. The Raman bands assignable to the stretching of the Pd–P bonds in complex **2** suggest a *cis* arrangement of the PPh_3 ligands. Several Pd^{II}-thionate-PPh_3 complexes with the phosphane ligands in *cis* positions have been reported by other research groups, with different coordination forms for the thionate ligands: chelating in $[Pd(\eta^2\text{-N,S-pym2S})(PPh_3)_2](ClO_4)$ [9e] or $[Pd(\eta^2\text{-N,S-py2S})(Cl)(PPh_3)]$ [9e, 9g]; bridging in $[Pd(\mu_2\text{-N,S-py2S})(Cl)(PPh_3)]_2$ [9d].

The UV/Vis spectra of complexes **2**–**5** as solid dispersed in KBr disks result very similar to each other. They show a weak broad band around 365 nm because of the π→π* transitions of the C–S_{exo} thiocarbonilic bond [29]. Other intense bands in the range 200–220 nm were assigned to the π→π* transitions of the benzene rings of the diphosphane ligands [34]. The spectra of CH_2Cl_2 solutions of compounds **3**–**5** show band displacements that can be attributed to solvent effects (Figure 4). Molar conductance of the complexes in CH_2Cl_2 solutions shows that they behave as molecular moieties. As a reference standard, we employed the ionic K(tsac) salt dissolved in MeCN. The solution showed a conductance of 120 $\Omega^{-1}\cdot mol^{-1}\cdot cm^{-1}$, which corresponds to a 1:1 electrolyte [35].

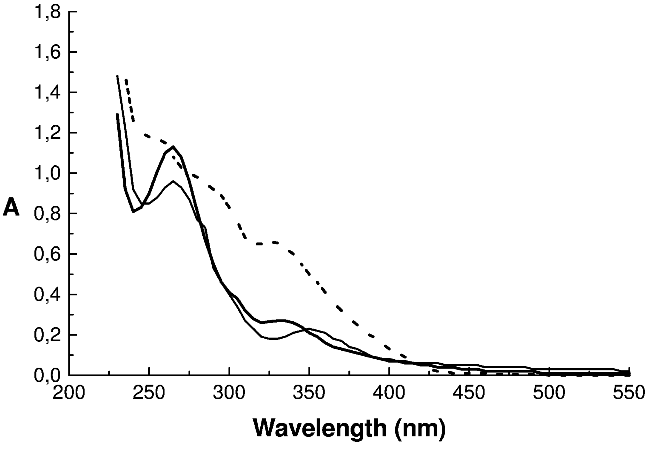


Figure 4. Electronic spectra of 2.0 × 10^{-5} m solutions in CH_2Cl_2: ——— $Pd(tsac)_2dppm$ (**3**); - - - - $Pd(tsac)_2(dppm)_2$ (**4**); ━━━ $Pd(tsac)_2dppe$ (**5**).

One of the characteristics of the monophosphane- and diphosphane-palladium chemistry is the existence of mononuclear/dinuclear rearrangement equilibria or dinuclear/dinuclear fluxional equilibria in solution. Several research groups determined the influence of several factors over those structural rearrangements, such as the temperature or the number of phosphine ligands and their structures, by using NMR spectroscopy [12f, 36]. There were several reports of pyridine-2-thionate complexes of the type $[Pd(\mu_2\text{-N,S-py2S})(Cl)(L)]_2$ [L = PMe_3, PMe_2Ph, $PMe(Ph)_2$], which exhibit dynamic behavior in solution in contrast to the closely related compounds $[Pd(\mu_2\text{-N,S-py2S})(Cl)(PPh_3)]_2$ and $[Pd(\eta^2\text{-N,S-py2S})(Cl)(PPh_3)]$ whose ^1H NMR spectrum shows a stereochemically rigid structure in solution [9e, 9f]. The room temperature ^1H and $^{31}P\{^1H\}$ NMR spectra of concentrated solutions of the complexes **3** and **5** in $[D_6]$DMSO were obtained and compared with the data of the corresponding free ligand. The presence of only one set of signals for both complexes confirms the existence of only one molecular species in solution without any mononuclear/dinuclear rearrangements equilibrium. The chemical shifts of the $^{31}P\{^1H\}$ NMR signals also indicate that the dppm or dppe molecules are still coordinated in solution. Unfortunately, because of the very low solubility of complex **2** in common organic solvents, its NMR spectra were of low quality and are not reported here.

Complex **4** is a little surprising compound. The chemical analysis and the vibration and electronic spectroscopic data are in agreement with a Pd^{II} complex with two thiosaccharinate ligands and two dppm molecules. The existence of one set of signals for the anions indicates that they are equivalent and tightly bonded to the metal atoms. The NMR analyses of the compound were necessary to understand the type of coordination of the dppm molecules. The $^{31}P\{^1H\}$ NMR spectra show two signals centered at 34 and 15 ppm, corresponding to one coordinated and one uncoordinated phosphorus atom, respectively. Therefore, a *cis*-$Pd(tsac)_2(\eta^1\text{-dppm})_2$ square planar structure is proposed for complex **4**.

Conclusions

The thiosaccharinate anion in its thiolate form strongly bond palladium atoms in +2 or +1 oxidation states. The structurally resolved palladium thiosaccharinates, $[Pd(tsac)_2(dppm)]$ and $[Pd(tsac)_2(dppe)]$, show a preferred η^1-S monocoordination form for the anions. In the presence of the strong soft bases PPh_3, dppm or dppe, the palladium(II) thiosaccharinate produces little soluble square-planar complexes with S_2P_2 coordination spheres.

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