Ring-Opening of Lawesson's Reagent: New Syntheses of Phosphono- and Amidophosphono-Dithioato Complexes − Structural and CP-MAS ^{31}P-NMR Characterization of [p-$CH_3OPh(X)PS_2]_2M$ (X = MeO, *i*PrNH; M = Ni^{II}, Pd^{II}, and Pt^{II})

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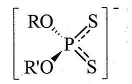
The opening of the P_2S_2 tetraatomic ring of Lawesson's reagent (**4**) has proved versatile in synthesizing phosphono- and amidophosphono-dithioato mononuclear complexes [p-$CH_3OPh(X)PS_2]_2M$ [X = CH_3O, *i*PrNH; M = Ni^{II}, Pd^{II}, Pt^{II}]. A one-step reaction of **4** with the appropriate metal salt in CH_3OH, or in the presence of a stoichiometric amount of *i*$PrNH_2$ in $CHCl_3$, is used in the direct synthesis of the Ni^{II} and Pd^{II} complexes, but does not work in the Pt^{II} complexes. Alternatively, these syntheses can be carried out: i) by preparation and isolation of *O*-methyl(4-methoxyphenyl)phosphonodithioate (**6**) salts or isopropylamido(4-methoxyphenyl)phosphonodithioate (**7**) salts by treating **4** with CH_3O^- in CH_3OH or with *i*$PrNH_2$, respectively; ii) by reaction of **6** or **7** with MCl_2 or K_2MCl_4 [M = Ni^{II}, Pd^{II}, Pt^{II}] to give *trans*-bis[*O*-methyl(4-methoxyphenyl)phosphonodithioato]M and *trans*-bis[isopropylamido(4-methoxyphenyl)phosphonodithioato]M complexes. Following these routes, *trans*-bis[*O*-methyl(4-methoxyphenyl)phosphonodithioato]M [M = Ni (**8a**), Pd (**8b**), and Pt (**8c**)] and *trans*-bis[isopropylamido(4-methoxyphenyl)phosphonodithioato]M [M = Ni (**9a**), Pd (**9b**), and Pt (**9c**)] complexes have been synthesized and fully characterized by FAB mass, FT-IR, FT-Raman, UV/Vis, and CP-MAS ^{31}P-NMR spectroscopy; the crystal structures of **7**, **8b**, **8c**, and **9a** are also reported.

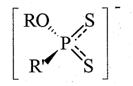
Introduction

Organophosphodithio compounds, such as phosphoro-,[1] phosphono-, and phosphanyl-dithioates[2] **1**, **2**, and **3** and corresponding metal complexes, play important roles in industrial and agricultural fields,[3] e.g. additives to lubricant oils,[4] extraction reagents for metal ions,[3,5] flotation agents for mineral ores,[3] insecticides,[3,6] rodenticides,[3,6] and pesticides.[3,6] Furthermore, phosphonate derivatives have assumed a great importance as a replacement of the phosphate moiety in biologically active molecules[7] in the past decades. Many papers have been published on the synthesis and coordination chemistry of **1** and **3**,[1,2,5,8] but, because of synthetic difficulties,[9] only a few have dealt with **2**.



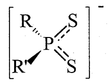
1

Phosphorodithioates



2

Phosphonodithioates



3

Phosphinodithioates

In fact, phosphonodithioate syntheses from organophosphanyl chlorides[9a] or P_4S_{10},[10] involve several laborious reaction steps. A synthesis of phosphonodithioic acid derivatives developed by Martin et al. involves the use of the appropriate Grignard reagent and 2-chloro-1,3,2-dithiaphospholane,[11] but several reaction steps are also required. Under the appropriate conditions, compounds such as 1,3-dithia-2,4-diphosphetane 2,4-disulfide derivatives can give a ring opening, as shown for the well-known Lawesson's reagent (**4**).[12] Although a large amount of information describing the reactivity of **4** can be found in the literature, very little can be found about the reactions of these substrates with transition metal ions[13] or main group elements.[14] We report two novel and facile synthetic routes for preparing complexes with type **2** ligands, i.e. phosphono- and amidophosphono-dithioate, p-$CH_3OPh(X)PS_2^-$, X = CH_3O, *i*PrNH, with Ni^{II}, Pd^{II}, and Pt^{II}.

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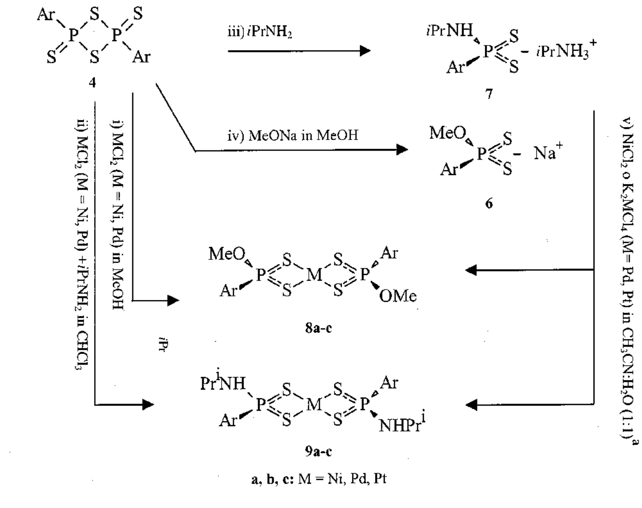
Results and Discussion

Reactivity

In an attempt to optimize the synthesis of a new class of nickel dithiolenes[15] using **4** as a sulfuring agent, we incidentally obtained Ni^{II} complexes of **2**, from which *trans*-bis[*O*-ethyl(4-methoxyphenyl)phosphonodithioate]Ni complex **5**, was structurally characterized;[21] this one-step reaction is shown in the pathway i) of Scheme 1. The ring opening of **4**, required in the formation of the complexes, requires a nucleophilic agent that is the same solvent, for example MeOH in i). Another way of inducing the ring opening of **4** to yield complexes is to use an amine in a stoichiometric amount relative to **4**, in an inert solvent in order to avoid competition reactions. Isopropylamine, $iPrNH_2$, has been chosen as a model compound and was used in $CHCl_3$ as shown in pathway ii). However, in both i) and ii) only phosphono- and amidophosphono-dithioate complexes of Ni^{II} (**8a**, **9a**) and Pd^{II} (**8b**, **9b**) were obtained, the former in higher yields than the latter. In contrast, in spite of several attempts, Pt^{II} complexes (**8c**, **9c**) were never obtained. To prepare Pt^{II} complexes, a different route was successfully attempted through the dithioato ligands **6** and **7**, see pathways iii), iv), and v). Here the two bases, sodium methoxide in MeOH and the amine working both as reagent and solvent, induce the ring opening of **4** to give phosphono- and amidophosphono-dithioate ligands **6** and **7**. As shown in pathway v), these ligands yielded phosphono- and amidophosphono-dithioato complexes **8a**–**8c** and **9a**–**9c**, respectively, almost quantitatively, when treated with $NiCl_2$ and K_2MCl_4 [M = Pd^{II}, Pt^{II}] in $MeCN/H_2O$. However, these experiments show that the difficulty in obtaining platinum complexes according to i) and ii) does not depend on their stabilities.



Ar = 4-methoxyphenyl. – [a] The reaction with K_2NiCl_4 has not been attempted.

Scheme 1

Crystal Structures

The crystal structures of **7**, **8b**, **8c**, and **9a** have been determined by single-crystal X-ray diffraction; ORTEP views of the structures together with atom-numbering schemes are shown for **7** (Figure 1), **8c** (Figure 2), and **9a** (Figure 3); some selected bond lengths and angles of **7**, **8b**, and **8c** are given in Table 1; those of compound **9c** in Table 2. The structures of the isostructural phosphonodithioates **8b** and **8c** consist of centrosymmetric square-planar complexes with the metal atom coordinated by the four S atoms of the two *S,S*-bidentate ligands. The two M–S bond lengths are comparable [Pd–S(1) and Pd–S(2) are 2.354(1) and 2.353(1) Å, Pt–S(1) and Pt–S(2) are 2.336(2) and 2.349(2) Å] as previously found for the similar (phosphonodithioato)nickel(II) complex **5** [2.220(1) and 2.222(1) Å].[21] The P atoms are in a pseudo-tetrahedral environment involving the carbon atom of the 4-methoxyphenyl group, the oxygen atom of the methoxy group, and the two S atoms. The P–S bond lengths [2.010(1) and 2.009 (1) Å for **8b**, and 2.011(3) and 2.010 (1) Å for **8c**] are also equal, suggesting a symmetrically delocalized P–S π bond. The P–S bond lengths are comparable with those found in **5**, in the *trans*-bis(*O*-ethylphenyl)phosphonodithioate of Ni,[9d] Pd,[9e] and

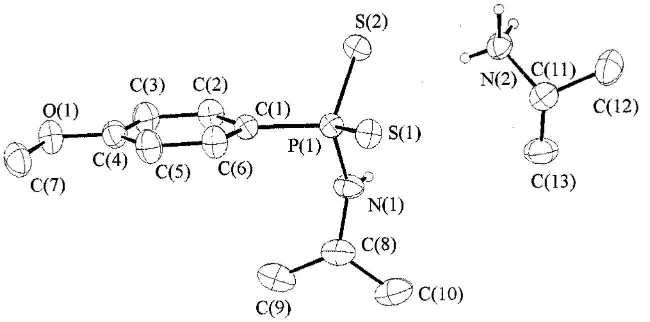


Figure 1. ORTEP drawing and atom-labeling scheme for the isopropylammonium salt of **7**; hydrogen atoms are partially omitted for clarity

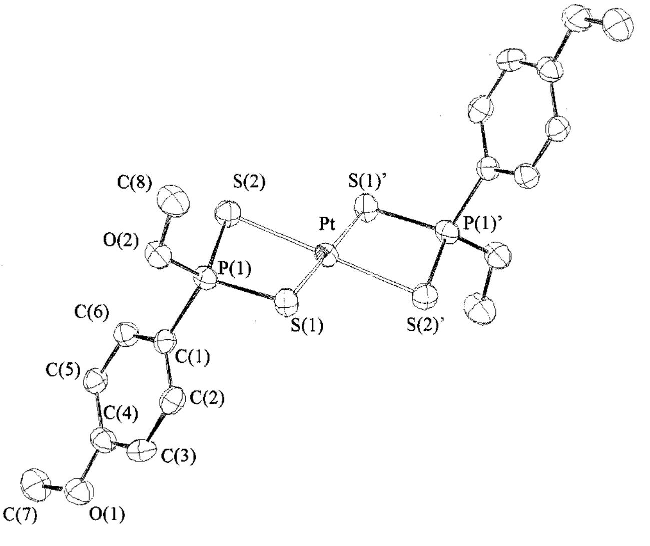


Figure 2. ORTEP drawing and atom-labeling scheme for compound **8c**; hydrogen atoms are omitted for clarity

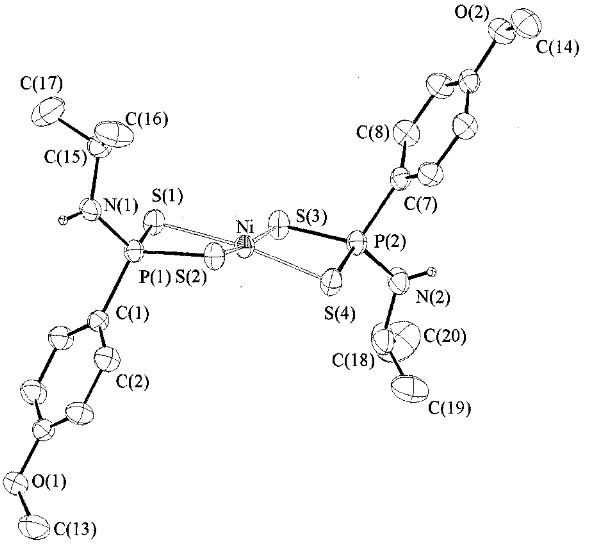


Figure 3. ORTEP drawing and atom-labeling scheme for compound **9a**; hydrogen atoms are partially omitted for clarity

Pt,[9e] and in analogous complexes with type **1** and **3** ligands,[8] and only differ from those found in *trans*-bis[(*O*-isopropyl)ethylphosphonodithioato]Ni[16] in which P−S single bonds, 2.031 Å, and P=S double bonds, 1.900 Å, are present.

The crystal structure of the *trans*-bis[isopropylamido(4-methoxyphenyl)phosphonodithioato]Ni complex **9a**, shows that the metal atom is coordinated by the four S atoms of two *S*,*S*-bidentate ligands. Also in this case, the four Ni−S bond lengths are comparable [2.225(2), 2.227(2), 2.228(2), and 2.216(2) Å], and the four P−S bond lengths [2.012(3), 2.016(3), 2.014(2), and 2.017(2) Å] are nearly identical, suggesting a delocalized P−S π bond, as for **8b** and **8c**. The structure of **9a** closely resembles that of **5**, where P−N bonds replace P−O bonds. The structure of **7**, which contains a unique example of an amidophosphonodithioate anion reported in the literature, displays structural features similar to those reported for type **1**[17] and **3**[18] salts, with similar P−S bond lengths [1.989(1) and 2.000(1) Å] according to a delocalization of the negative charge over the S−P−S fragment. A significant difference between the values of the two P−S bonds [1.945(2) and 1.969(2) Å] has only been found in the case of $K[S_2P(OCH_2Ph)_2]$.[17a] The P−N bond length [1.655(3) Å] in **7** is appreciably longer than those found in **9a** [1.619(4) and 1.622(4) Å].

Table 1. Selected bond lengths [Å] and angles [°] for the isopropylammonium salt of **7**

	7 salt[a]	**8b**[b]	**8c**[c]
M−S(1)	−	2.340(1)	2.336(2)
M−S(2)	−	2.354(1)	2.349(2)
C(4)−O(1)	1.369(4)	1.362(4)	1.355(9)
P(1)−X	1.655(3)	1.583(3)	1.583(5)
S(1)−P(1)	1.989(1)	2.010(1)	2.011(3)
S(2)−P(1)	2.000(1)	2.009(1)	2.010(3)
C(1)−P(1)	1.816(3)	1.784(4)	1.792(8)
C(8)−X	1.466(4)	1.467(7)	1.456(9)
S(1)−M−S(1)′	−	180.0	180.0
S(1)−M−S(2)	−	85.23(4)	84.47(8)
S(1)−M−S(2)′	−	94.77(4)	95.53(8)
P(1)−S(1)−M	−	83.58(5)	84.3(1)
P(1)−S(2)−M	−	83.26(5)	83.9(1)
X−P(1)−C(1)	104.5(1)	101.2(2)	101.5(3)
X−P(1)−S(1)	112.5(1)	112.9(1)	113.6(3)
X−P(1)−S(2)	107.0(1)	113.4(1)	113.7(3)
S(2)−P(1)−S(1)	114.29(5)	104.54(6)	103.1(1)
C(1)−P(1)−S(1)	109.6(1)	113.0(1)	113.7(3)
C(2)−C(1)−P(1)	119.2(2)	119.6(3)	120.0(6)
C(6)−C(1)−P(1)	122.7(2)	121.3(3)	122.0(7)
C(1)−C(2)−C(3)	120.9(3)	119.5(4)	120.6(8)
C(8)−X−P(1)	123.5(2)	119.0(3)	119.8(5)

[a] X = N(1); ′ = −*x*, −*y*, −*z*. − [b] M = Pd; X = O(2). − [c] M = Pt; X = O(2).

Table 2. Selected bond lengths [Å] and angles [°] for compound **9a**

Ni(1)−S(4)	2.216(2)	S(4)−Ni(1)−S(2)	92.37(6)
Ni(1)−S(1)	2.225(2)	S(1)−Ni(1)−S(2)	87.65(6)
Ni(1)−S(2)	2.227(2)	S(4)−Ni(1)−S(3)	87.62(6)
Ni(1)−S(3)	2.228(2)	S(1)−Ni(1)−S(3)	93.25(5)
S(1)−P(1)	2.012(2)	P(1)−S(1)−Ni(1)	84.93(6)
S(2)−P(1)	2.016(2)	P(1)−S(2)−Ni(1)	84.79(6)
S(3)−P(2)	2.014(2)	P(2)−S(3)−Ni(1)	84.94(6)
S(4)−P(2)	2.017(2)	P(2)−S(4)−Ni(1)	85.19(6)
P(1)−N(1)	1.619(4)	N(1)−P(1)−C(1)	103.0(2)
P(2)−N(2)	1.622(4)	N(1)−P(1)−S(1)	114.9(2)
N(1)−H(1N)	0.76(4)	N(1)−P(1)−S(2)	114.2(2)
N(2)−H(2N)	0.85(5)	S(1)−P(1)−S(2)	99.84(7)
		N(2)−P(2)−C(7)	102.6(2)
		N(2)−P(2)−S(3)	114.0(2)
		N(2)−P(2)−S(4)	116.0(2)
		S(3)−P(2)−S(4)	99.49(7)
		C(15)−N(1)−P(1)	124.5(4)
		C(18)−N(2)−P(2)	124.2(4)
		P(2)−N(2)−C(18)	124.2(4)

CP-MAS ^{31}P NMR

Sodium *O*-methyl(4-methoxyphenyl)phosphonodithioate shows a signal at δ = 110.4, which is expectedly different from the value observed for the isopropylammonium isopropylamido(4-methoxyphenyl)phosphonodithioate (δ = 72.7). This value is comparable with the previously reported value for methylammonium methylamido(4-methoxyphenyl)phosphonodithioate (δ = 82.3), which was measured in methylamine solution.[19] Analogous differences are also observed for the corresponding Ni, Pd, and Pt complexes of the two classes of ligands; the ^{31}P-NMR chemical shift for **8a−c** (δ = 97.3, 110.2, 105.7, respectively) was always found downfield relative to those measured for **9a−c** (δ = 71.7, 84.1, 81.7, respectively). The observation that the variation of the S−P−S bond angle affects the ^{31}P chemical shifts[20] seems to be confirmed by these measurements. In fact, within the same series (e.g. **5**, **8b**, **8c**, and **7**, **9a**), a bigger value of the ^{31}P-NMR chemical shift corresponds to an increase in the bond angle.

Conclusions

The easy one-step reaction between Lawesson's reagent (**4**) and alcohols ROH or amines $R'NH_2$ leads to phosphono- and amido-phosphonodithioato ligands (**6** and **7** for R = Me and R′ = *i*Pr, respectively). From these ligands, the corresponding Ni^{II}, Pd^{II}, and Pt^{II} complexes (**8a−c**, **9a−c**) have been synthesized and fully characterized by means of spectroscopic and diffractometric techniques. The mild reaction conditions and high yields allow the introduction of the desired groups in the phosphono- and amidophosphono-dithioato ligands. This opens interesting perspectives in obtaining novel materials starting from alcohols and amines having intrinsic peculiarities.

Experimental Section

General: All reagents and solvents were purchased from Aldrich or Merck and used without further purification. − Elemental analyses were performed with an EA1108 CHNS-O Fisons instrument. − Infrared spectra were recorded with a Bruker IFS55 spectrometer at room temperature using a flow of dried air. Far-IR (500−50 cm^{-1}) spectra (resolution 2 cm^{-1}) were recorded as polythene pellets with a Mylar beam-splitter and polythene windows. Middle IR spectra (resolution 2 cm^{-1}) were recorded as KBr pellets, with a KBr beam-splitter and KBr windows. − FT-Raman spectra were recorded with a resolution of 2 cm^{-1} using a Bruker RFS100 FT-Raman spectrometer, fitted with an In−Ga−As detector (room temperature) operating with an Nd-YAG laser (excitation wavelength 1064 nm) with a 180° scattering geometry. The excitation power was modulated between 100 and 250 mW. − CP-MAS solid-state ^{31}P-NMR spectra were recorded with a Varian Unity Inova 400-MHz instrument operating at 161.9 MHz with samples packed into a zirconium oxide rotor. The ^{31}P-NMR chemical shifts were calibrated indirectly through the 85% H_3PO_4 peak (δ = 0.0).

(4-Methoxyphenyl)-*O*-methylphosphonodithioate (6), Sodium Salt: A mixture of MeONa (0.76 g, 15 mmol) and **4** (3.00 g, 7.42 mmol) in methanol was heated at reflux for 1 h, and the solvent was then removed under reduced pressure to give a white solid (3.41 g, 90%). − M.p. > 290 °C with decomposition. − $C_8H_{10}NaO_2PS_2$ (256.2): calcd. C 37.5, H 3.9, S 25.0; found C 36.7, H 4.2, S 24.2. − FAB mass spectrum (gly/MeOH/H_2O matrix); *m*/*z*: 233; calcd. for $C_8H_{10}O_2PS_2$ 233 with correct isotopic distribution. − FT-IR (3500−100 cm^{-1}): 3060vw, 3006vw, 2936w, 2833w, 2091w, 1601vs, 1570s, 1501vs, 1466m, 1441m, 1403m, 1383w, 1298s, 1261vs, 1179s, 1152w, 1131w, 1113s, 1106s, 1150w, 1025m, 996vs, 831s, 802m, 748vs, 671vs, 629m, 559s, 511m, 474m, 466w, 437w, 382m, 227w cm^{-1}. − FT-Raman (3500−50 cm^{-1}; relative intensities in parentheses related to the highest peak taken equal to 10.0): 3065 (4.0), 3014 (1.8), 2933 (1.9), 2833 (1.9), 1592 (5.4), 1450 (1.3), 1185 (1.8), 1107 (6.7), 1006 (1.3), 801 (4.9), 654 (2.2), 627 (2.7), 559 (6.9), 523 (1.9), 414 (2.8), 388 (5.4), 364 (2.3), 255 (2.7), 194 (2.7), 92 (10) cm^{-1}. − CP-MAS ^{31}P NMR: δ = 110.4 (s), 111.1 (s), 113.8 (s).

Isopropylamido(4-methoxyphenyl)phosphonodithioate (7), Isopropylammonium Salt: A weighed amount of **4** (1.60 g, 3.96 mmol) was stirred in isopropylamine (50 mL). After a few minutes, the solvent was removed under reduced pressure to give the salt as a white solid (1.28 g, quantitative). Crystals suitable for X-ray analysis were grown from an isopropylamine solution. − M.p. 175 °C. − $C_{13}H_{25}N_2OPS_2$ (320.4): calcd. C 48.7, H 7.9, N 8.7, S 20.0; found C 49.4, H 8.2, N 9.0, S 20.3. − FAB mass spectrum (3-NOBA matrix); *m*/*z*: 321; calcd. for $C_{13}H_{25}N_2OPS_2$ 320 with correct isotopic distribution. − FT-IR (3500−100 cm^{-1}): 3328m, 3000mbr, 1597vs, 1571s, 1497vs, 1466s, 1392m, 1303s, 1294s, 1250vs, 1175s, 1161m, 1135m, 1101s, 1032s, 1004s, 831s, 815m, 798m, 647vs, 622vs, 562vs, 460w cm^{-1}. − FT-Raman (3500−50 cm^{-1}; relative intensities in parentheses related to the highest peak taken equal to 10.0): 3329 (0.9), 3062 (3.3), 2978 (4.2), 2941 (3.5), 2880 (1.7), 2839 (1.4), 1593 (3.8), 1465 (1.5), 1302 (1.4), 1183 (1.8), 1101 (5.4), 798 (4.0), 624 (1.7), 623 (1.9), 566 (5.9), 522 (2.2), 114 (5.9), 69 (10.0) cm^{-1}. − CP-MAS ^{31}P NMR: δ = 72.7 (s).

***trans*-Bis[(4-methoxyphenyl)-*O*-methylphosphonodithioato]Ni (8a):** The synthesis, melting point, and elemental analysis of **8a** have already been reported.[20] − FAB mass spectrum (3-NOBA matrix); *m*/*z*: 524; calcd. for ^{58}Ni 524 with correct isotopic distribution. − Electronic spectrum in CH_2Cl_2: 248 (30820), 328 (22890), 388 (1660), 536 (110), 694 nm (100 M^{-1} cm^{-1}). − FT-IR (3500−100 cm^{-1}): 2997vw, 2941vw, 2837vw, 1597vs, 1567w, 1500s, 1440w, 1307m, 1294s, 1269vs, 1177s, 1165vw, 1118vs, 1029m, 1011s, 1003vs, 836m, 789vs, 667s, 640s, 622m, 550s, 524m, 435m, 375m, 351m, 297w, 277vw, 202vw, 165vw cm^{-1}. − FT-Raman (3500−50 cm^{-1}; relative intensities in parentheses related to the highest peak taken equal to 10.0): 3074 (3.8), 2998 (2.1), 2943 (3.8), 2838 (1.4), 1590 (6.3), 1566 (1.2), 1259 (1.2), 1118 (7.2), 1002 (1.2), 801 (2.8), 667 (2.6), 639 (3.3), 553 (9.1), 491 (1.2), 440 (1.3), 314 (6.1), 296 (1.7), 278 (1.7), 238 (2.6), 102 (9.7), 84 (10.0) cm^{-1}. − CP-MAS ^{31}P NMR: δ = 97.3 (s).

***trans*-Bis[(4-methoxyphenyl)-*O*-methylphosphonodithioato]Pd (8b):** The complex has been synthesized according to reaction (iii) (a) or reaction (v) (b) in Scheme 1. − (a): A mixture of $PdCl_2$ (0.30 g, 1.7 mmol) and **4** (0.70 g, 1.7 mmol) in methanol (60 mL) was heated at reflux for 2 h, and the solvent was then removed under reduced pressure. The resulting orange solid was washed with CH_3CN and dried under vacuum (0.84 g, yield 86%). − (b): A CH_3CN/H_2O solution (1:1, v/v, 10 mL) of K_2PdCl_4 (0.2 g, 0.6 mmol) was added dropwise to a sodium salt solution of **6** (0.56 g, 2.2 mmol) in the same mixture of solvents. After heating at reflux for 2 h, the resulting orange solid was filtered off, washed with the same mixture of solvents, and vacuum-dried (0.21 g, 60%). Crystals suitable for X-ray diffraction analysis were grown by slow evaporation of a 1:1 $CHCl_3/CH_3OH$ solution. − M.p. 203 °C. − $C_{16}H_{20}O_4P_2PdS_4$ (572.9): calcd. C 33.5, H 3.5, S 22.4; found C 33.7, H 3.7, S 22.2. − FAB mass spectrum (3-NOBA matrix); *m*/*z*: 572; calcd. for ^{106}Pd 572 with correct isotopic distribution. − Electronic spectrum in $CHCl_3$: 248 (22530), 302 (31480), 352 (4310), 474 nm (380 M^{-1} cm^{-1}). − FT-IR (3500−100 cm^{-1}): 3002vw, 2965vw, 2943w, 2837vw, 1595vs, 1566m, 1502s, 1442m, 1407w, 1309m, 1296s, 1263vs, 1181s, 1117vs, 1027s, 1012vs, 1002vs, 829m, 792vs, 664s, 636m, 611s, 545vs, 525m, 430m, 372w, 348w, 313s, 200vw, 168vw cm^{-1}. − FT-Raman (3500−50 cm^{-1}; relative intensities in parentheses related to the highest peak taken equal to 10.0): 3071 (1.5), 3004 (1.2), 2943 (2.5), 2839 (2.0), 1591 (5.4), 1116 (6.9), 800 (3.5), 668 (2.5), 637 (3.0), 611 (1.6), 548 (10.0), 523 (1.7), 484 (1.9), 432 (2.5), 374 (1.2), 326 (9.4), 275 (2.1), 186 (1.6), 114 (8.0), 84 (3.1) cm^{-1}. − CP-MAS ^{31}P NMR: δ = 110.2 (s).

***trans*-Bis[(4-methoxyphenyl)-*O*-methylphosphonodithioato]Pt (8c):** A solution of K_2PtCl_4 (0.2 g, 0.6 mmol) in CH_3CN/H_2O (1:1, v/v, 10 mL) was added dropwise to a solution of the sodium salt of **6** (0.56 g, 2.2 mmol) in the same mixture of solvents (40 mL). After heating at reflux for 1.5 h, the resulting yellow solid was filtered off, washed with the same mixture of solvents, and vacuum-dried (0.29 g, 73%). Crystals of **8c** were prepared by slow evaporation of a CH_2Cl_2/CH_3OH (1:1) mixture. − M.p. 189 °C. − $C_{16}H_{20}O_4P_2PtS_4$ (661.6): calcd. C 29.0, H 3.0, S 19.4; found C 29.4, H 3.0, S 19.7. − FAB mass spectrum (3-NOBA matrix); *m*/*z*: 661; calcd. for ^{195}Pt 661 with correct isotopic distribution. − Electronic spectrum in CH_2Cl_2: 258 (33700), 294 (9260), 418 nm (170 M^{-1} cm^{-1}). − FT-IR (3500−100 cm^{-1}): 3007vw, 2965w, 2940m, 2837w, 1595s, 1566m, 1502s, 1458w, 1309m, 1297m, 1264s, 1183m, 1118vs, 1026m, 1011vs, 1003vs, 829m, 795vs, 665s, 636m, 612s, 545s, 526w, 429m, 374w, 303m cm^{-1}. − FT-Raman (3500−50 cm^{-1}; relative intensities in parentheses related to the highest peak taken equal to 10.0): 3074 (2.1), 2943 (2.6), 1590 (5.1), 1566 (1.1), 1308 (1.3), 1257 (0.9), 1185 (1.3), 1117 (8.7), 802 (4.8), 667 (2.6), 637 (1.7), 612 (1.6), 547 (10.0), 523 (1.7), 482 (2.2), 432 (3.0), 342 (4.2), 316 (3.5), 282 (2.1), 188 (3.1), 127 (10.0), 82 (8.6) cm^{-1}. − CP-MAS ^{31}P NMR: δ = 104.4 (s), 105.7 (s).

***trans*-Bis[*N*-isopropyl(4-methoxyphenyl)amidophosphonodithioato]Ni (9a):** A mixture of **4** (1.7 g, 4.2 mmol) and $NiCl_2 \cdot 6\,H_2O$ (1.0 g, 4.2 mmol) in isopropylamine was heat at reflux for 48 h, and the solvent removed under reduced pressure. The residue was dissolved in $CHCl_3$, and the resulting solution was cooled to −18 °C after filtration. The obtained purple solid was filtered off, dried under vacuum, and recrystallized from CH_2Cl_2. The yield was quantitative (2.4 g). Crystals of **9a** were obtained by diffusion of Et_2O vapors into a CH_2Cl_2 solution. − M.p. 175 °C with decomposition. − $C_{20}H_{30}N_2NiO_2P_2S_4$ (579.4): calcd. C 41.5, H 5.2, N 4.8, S 22.1; found C 41.4, H, 5.5 N 4.9, S 22.1. − FAB mass spectrum (3-NOBA matrix); *m*/*z*: 578; calcd. for ^{58}Ni 578 with correct isotopic distribution. − Electronic spectrum in CH_2Cl_2: 246 (29900), 328 (21600), 388 (1410), 528 (120), 686 nm (100 M^{-1} cm^{-1}). − FT-IR (3500−100 cm^{-1}): 3334m, 3024w, 2967w, 1595vs, 1572m, 1499s, 1453m, 1405m, 1383m, 1292w, 1250vs, 1181m, 1130wsh, 1115vs, 1020s, 893m, 814wsh, 806m, 608m, 547s, 528m, 386w, 353m, 281w, 202w, 153w, 121vw cm^{-1}. − FT-Raman (3500−50 cm^{-1}; relative intensities in parentheses related to the highest peak taken as equal to 10.0): 3057 (1.3), 2969 (1.3), 1595 (2.7), 1179 (1.4), 1114 (4.2), 800 (1.5), 661 (1.0), 634 (1.6), 600 (1.0), 550 (6.0), 313 (3.5), 164 (5.5), 103 (10.0) cm^{-1}. − CP-MAS ^{31}P NMR: δ = 71.7 (s).

***trans*-Bis[*N*-isopropyl(4-methoxyphenyl)amidophosphonodithioato]Pd (9b):** A solution of K_2PdCl_4 (0.2 g, 0.6 mmol) in CH_3CN/H_2O (1:1, v/v, 10 mL) was added dropwise to a solution of the isopropylammonium salt of **7** (0.7 g, 2 mmol) in the same mixture of solvents (40 mL). The product was obtained quantitatively (0.4 g) as an orange solid, which was filtered off, washed with the same mixture of solvents, vacuum-dried, and recrystallized from a $CHCl_3/CH_3OH$ mixture (1:1, v/v). − M.p. 205 °C. − $C_{20}H_{30}N_2O_2P_2PdS_4$ (627.1): calcd. C 38.3, H 4.8, N 4.5, S 20.4; found C 38.6, H 5.0, N 4.5, S 19.9. − FAB mass spectrum (3-NOBA matrix); *m*/*z*: 626; calcd. for ^{106}Pd 626 with correct isotopic distributions. − Electronic spectrum in $CHCl_3$: 248 (27400), 304 (34500), 352 (4500), 470 nm (320 M^{-1} cm^{-1}). − FT-IR (3500−100 cm^{-1}): 3337m, 3024vw, 2959w, 2868vw, 2836vw, 1595s, 1571w, 1495s, 1455w, 1405m, 1293w, 1250vs, 1181m, 1164w, 1130wsh, 1113vs, 1019s, 895m, 828w, 815m, 807m, 659m, 599m, 542s, 529w, 470w, 462vw, 393w, 384w, 314m, 278vw, 150vw cm^{-1}. − FT-Raman (3500−50 cm^{-1}; relative intensities in parentheses related to the highest peak taken equal to 10.0): 3339 (0.5), 3091 (0.8), 3056 (2.4), 3027 (2.4), 2959 (2.0), 2928 (1.4), 1585 (4.1), 1458 (0.8), 1303 (0.8), 1248 (1.1), 1178 (2.0), 1113 (5.7), 1026 (0.6), 897 (0.5), 800 (1.9), 660 (1.1), 623 (1.9), 596 (1.6), 544 (6.3), 436 (1.0), 397 (1.3), 384 (1.4), 327 (6.4), 292 (2.1), 231 (1.7), 164 (7.9), 126 (4.6), 105 (10.0) cm^{-1}. − CP-MAS ^{31}P NMR: δ = 84.1 (s).

***trans*-Bis[*N*-isopropyl(4-methoxyphenyl)amidophosphonodithioato]Pt, (9c):** A solution of K_2PtCl_4 (0.25 g, 0.60 mmol) in CH_3CN/H_2O (1:1, v/v, 10 mL) was added dropwise to a solution of the isopropylammonium salt of **7** (0.37 g, 1.2 mmol) in the same mixture of solvents (40 mL). After heating at reflux for 2 h, the resulting yellow solid was filtered off, washed with the same mixture of solvents, and vacuum-dried (0.33 g, yield 76%). Crystals of **9c** were grown by slow evaporation of a 1:1 CH_2Cl_2/CH_3OH mixture. − M.p. 205 °C. − $C_{20}H_{30}N_2O_2P_2PtS_4$ (715.7): calcd. C 33.6, H 4.2, N 3.9; S 17.9; found C 33.8, H 4.2, N 4.0, S 17.8. − FAB mass spectrum (3-NOBA matrix); *m*/*z*: 715; calcd. for ^{195}Pt 715 with correct isotopic distribution. − Electronic spectrum in $CHCl_3$: 258 (32300), 298 (8980), 422 nm (230 M^{-1} cm^{-1}). − FT-IR (3500−100 cm^{-1}): 2960w, 2920vw, 2867vw, 2835vw, 1594s, 1570w, 1497s, 1455w, 1440vw, 1404m, 1383w, 1293m, 1249vs, 1181m, 1164w, 1112vs, 1019vs, 895m, 827vw, 814s, 807s, 658m, 598m, 540s,

Table 3. Summary of X-ray single-crystal data and structure refinement parameters for the isopropylammonium salt of **7**, **8b**, **8c**, and **9a**

	7 (salt)	**8b**	**8c**	**9a**[a]
Empirical formula	$C_{13}H_{25}N_2OPS_2$	$C_{16}H_{20}O_4P_2PdS_4$	$C_{16}H_{20}O_4P_2PtS_4$	$C_{20}H_{30}N_2NiO_2P_2S_4$
Molecular mass	320.44	572.94	661.59	579.35
Temperature [K]	293(2)	293(2)	293(2)	293(2)
Crystal system	triclinic	monoclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a [Å]	9.134(3)	11.934(4)	11.912(4)	11.196(4)
b [Å]	15.923(5)	6.580(3)	6.554(3)	12.557(5)
c [Å]	6.302(3)	14.609(4)	14.664(4)	11.095(4)
α [°]	95.84(4)	90	90	92.04(4)
β [°]	97.47(4)	108.59(2)	108.73(2)	104.75(5)
γ [°]	101.11(5)	90	90	114.92(5)
Volume [Å^3]	884.1(6)	1087.3(8)	1084.2(8)	1349.7(10)
Z	2	2	2	2
D_c [g cm^{-3}]	1.204	1.75	2.027	1.43
Wavelength [Å]	1.54184 (Cu-K_α)	0.71073 (Mo-K_α)	0.71073 (Mo-K_α)	1.54184 (Cu-K_α)
F (000)	344	576	640	604
θ range [°]	3−70	3−25	3.44−28.12	3−70
Unique refl. with $I > 2\sigma(I)$	3356	1654	2633	5121
Final *R*1, *wR*2 indices[b]	0.053, 0.151	0.029, 0.036	0.036, 0.071	0.048, 0.120
No. of variables	272	124	127	289
GOF	1.021	0.877	0.757	0.742
Min/max height in final Δρ map [eÅ^{-3}]	−0.48/0.53	−0.22/0.38	−1.58/1.06	−0.39/0.48

[a] The cell parameters of **9c** have also been measured: triclinic, space group $P\bar{1}$, $a = 11.173(2)$, $b = 12.640(4)$, $c = 11.266(3)$ Å, α = 91.06 (3), β = 104.67(2), γ = 115.72(1)°. The reflections have not been collected, since **9c** is isostructural with **9a**. − [b] $R1 = \Sigma|F_o - F_c|/|\Sigma(F_o)|$; $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

494vw, 393vw, 382vw, 308m cm^{-1}. − FT-Raman (3500−50 cm^{-1}; relative intensities in parentheses related to the highest peak taken equal to 10.0): 3057 (3.2), 2959 (2.8), 2927 (1.9), 1594 (5.3), 1459 (1.2), 1247 (1.5), 1179 (2.7), 1121 (7.2), 800 (2.4), 659 (1.4), 631 (1.8), 542 (8.2), 463 (1.3), 399 (1.8), 383 (1.7), 349 (2.1), 316 (3.3), 234 (1.5), 169 (5.0), 103 (10.0) cm^{-1}. − CP-MAS ^{31}P NMR: δ = 81.7 (s).

X-ray Structure Determination of 7 (Isopropylammonium Salt), 8b, 8c, and 9a: Crystallographic and experimental details of the data collection and refinement of the structures of **7** (isopropylammonium salt), **8b**, **8c**, and **9a** are reported in Table 3, while the molecular structures are depicted in Figures 1−3. The intensity data of the salt of **7** and **9a** were collected with an Enraf−Nonius CAD-4 single-crystal diffractometer, using the graphite-monochromated Cu-K_α radiation and the $\theta/2\theta$ scan technique. The intensity data of **8c** were collected with a Siemens AED single-crystal diffractometer, using graphite-monochromated Mo-K_α radiation and the $\theta/2\theta$ scan technique. The intensity data of **8b** were collected with a CAD-4 single-crystal diffractometer, using graphite-monochromated Mo-K_α radiation and the ω scan technique. Data were corrected in the usual manner for Lorentz and polarization effects, as well as for absorption.[22,23] − The structures were solved by Patterson and Fourier methods, and refined by full-matrix least-squares procedures based on F_o^2, first with isotropic displacement parameters, and then with anisotropic displacement parameters in the last cycles of refinement for all non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions, and refined "riding" on the corresponding carbon atoms for **8b**, **8c**, and **9a**; in the case of **7** (isopropylammonium salt), the hydrogen atoms were clearly found in the ΔF map and refined isotropically. − All calculations were performed using the SHELXS[24] and SHELXL[25] systems of crystallographic computer programs. − Lists of atomic coordinates for the non-H atoms, coordinates for the hydrogen atoms, and anisotropic displacement parameters, crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publications nos. CCDC-140139 (**7** isopropylammonium salt), -140140 (**8b**), -140141 (**8c**), and -140142 (**9a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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