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PLATINUM(II) COMPLEXES WITH DITHIOLATES AND PHOSPHINITES AS LIGANDS: CRYSTAL STRUCTURE OF $[Pt\{S_2CO\}\{P(OMe)Ph_2\}_2]$

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Abstract—Reaction of the complex $[PtCl\{P(O)Ph_2\}\{P(OH)Ph_2\}_2]$ with silver or thallium derivatives of dithiolate ligands led to neutral complexes of general formula $[Pt\{S—S\}\{P(O)Ph_2\}\{P(OH)Ph_2\}]$, where $\{S—S\}^- = \{S_2CNEt_2\}^-$ (**1**), $\{S_2P(OEt)_2\}^-$ (**2**) and $\{S_2COEt\}^-$ (**3**). Complexes **2** and **3** reacted with an excess of NaI in acetone solution by dealkylation of the coordinated dithiolate ligand and formation of the compounds $[Pt\{S_2P(O)(OEt)\}\{P(O)Ph_2\}\{P(OH)Ph_2\}]Na$ (**4**) and $[Pt\{S_2CO\}\{P(O)Ph_2\}\{P(OH)Ph_2\}]Na$ (**5**), respectively. The corresponding tetraphenylphosphonium derivatives (**6**, **7**) were prepared by a metathetical reaction of these complexes with Ph_4PBr in acetone solution. Related dithiolate complexes were obtained by reaction of the complex $[Pt\{S—S\}_2]$ with $P(OMe)Ph_2$ in molar ratio 1:2. Thus, the reaction of $[Pt\{S_2COEt\}_2]$ in dichloromethane solution at room temperature gave $[Pt\{S_2COEt\}\{P(OMe)Ph_2\}_2]Cl$ (**8**). This complex reacted with NaI in acetone to form the neutral compound $[Pt\{S_2CO\}\{P(OMe)Ph_2\}_2]$ (**9**). When the reaction was carried out in dichloromethane at reflux temperature using $[Pt\{S_2P(OEt)_2\}_2]$ as starting material, the neutral compound $[Pt\{S_2P(O)(OEt)\}\{P(OMe)Ph_2\}_2]$ (**10**) was obtained. The crystal structure of the complex **9** has been determined by X-ray diffraction. The neutral complex shows a nearly square-planar coordination of the metal and a planar dithiocarbonate ligand.

The coordination chemistry of platinum in its oxidation state of II or IV is largely due to the great stability of its complexes, with mono-, bi- or polydentate ligands.[1] Nevertheless, there are few examples of compounds of platinum(II) having connecting phosphinites $[P(O)Ph_2]$, phosphonates $[P(O)(OR)_2]$ and dithiolate groups as ligands. The complexes containing simultaneously a secondary phosphonito or phosphonate and a secondary phosphinous acid or phosphite as ligands in a *cis* arrangement have been the subject of increasing interest due to the presence of a symmetrical hydrogen system, where the hydrogen-bonded proton can easily be removed to form a bis(phosphinite) or phosphonate complex which can act as a bidentate chelating ligand through the oxygen atoms.[2]

Some neutral mono- or binuclear compounds containing phosphinite ligands, such as $[Pt\{P(O)Ph_2\}_2\{P(OH)Ph_2\}_2]$,[3] $M_2(\mu\text{-}X_2)\{P(O)Ph_2\}_2\{P(OH)$

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$Ph_2\}_2]$, $[MX\{P(O)Ph_2\}\{P(OH)Ph_2\}_2]$[4] ($M = Pd^{II}$, Pt^{II}; X = Cl, Br), and similar neutral or cationic phosphonate complexes of general formula $[Pt\{P(O)(RO)_2\}_2\{P(OH)(RO)_2\}_2]$, $[(R'_3P)ClPt\{P(O)(RO)_2\}\{P(OH)(RO)_2\}]$[2,5] (R′ = Et, Ph; R = Me, Et, Ph) and $[\{CH_2(Ph_2P)_2\}Pt\{P(O)(MeO)_2\}_2]$,[6] have been described.

On the other hand, the synthesis and properties of mixed ligand complexes containing phosphinite and dithiolate groups, or phosphonate and chalcogenide ligands derived from tertiary phosphines of the types $[(Me_2PS_2)Pd\{P(O)Ph_2\}\{P(OH)Ph_2\}]$, $[\{Et_2NCS_2\}Pt\{P(O)Ph_2\}\{P(OH)Ph_2\}]$,[7] $[Pt\{S_2CNR_2\}\{P(OH)Ph_2\}\{P(S)Ph_2\}]$[8] ($R = Et, Pr^i$) and $[M\{P(O)(OR)_2\}\{P(OH)(OR)_2\}\{CH_2(Ph_2PE)_2\}]BF_4$[9] ($M = Pd^{II}, Rh^{I}$, R = Me, Et and E = S or Se), have been described.

In this paper, we report the synthesis of platinum(II) compounds that contain phosphinites $[Ph_2P(O)]$ and dithiolates $[Et_2NCS_2^-, (EtO)_2PS_2^-$ or $EtOCS_2^-]$ as ligands, by a metathetical reaction of the complex $[PtCl\{P(O)Ph_2\}\{P(OH)Ph_2\}_2]$ with the corresponding silver or thallium salts of the dithiolate ligands. The molecular structure of the complex $[Pt\{S_2CO\}\{P(OMe)Ph_2\}_2]$, determined by single-crystal X-ray diffraction, is also reported.

EXPERIMENTAL

The syntheses were performed under purified nitrogen with standard Schlenk techniques. The starting complexes $[Pt(S_2CNEt_2)_2]$,[10] $[Pt\{S_2P(EtO)_2\}_2]$[11] and $[PtCl\{P(O)Ph_2\}\{P(OH)Ph_2\}_2]$[4] were prepared by published procedures.

Elemental analyses were made with a Heraeus Mikro Standard microanalyser. IR spectra were recorded on a Perkin–Elmer 567 spectrophotometer (over the 4000–200 cm^{-1} range) using KBr pellets. Conductivities were measured in *ca* 10^{-5} M acetone solution using a WTW LF-521 conductimeter. NMR [^1H (200 MHz), $^{31}P\{^1H\}$ (81 MHz), $^{13}C\{^1H\}$ (50 MHz), 20°C] spectra were recorded on a Bruker AC200P spectrometer; the chemical shifts are reported relative to $SiMe_4$ and 85% H_3PO_4 in D_2O (positive shifts downfield).

Preparation of $[TlS_2COEt]$

A solution of $TlNO_3$ (675 mg; 2.5 mmol) in water (25 cm^3) was treated with an aqueous solution of KS_2COEt (406 mg; 2.5 mmol). After stirring the solution for 1 h, the solid formed was filtered, washed with water and dried *in vacuo*. The solid obtained was crystallized as air-stable yellow crystals from acetone–diethyl ether. Yield 0.78 g (95%). Found: C, 11.7; H, 1.9. Calc. for $C_3H_5OS_2Tl$: C, 11.1; H, 1.5%.

Preparation of $[Pt(S{-}S)\{P(O)Ph_2\}\{P(OH)Ph_2\}]$ $[(S{-}S)^- = (S_2CNEt_2)^-$ (**1**), $(S_2P(OEt)_2)^-$ (**2**)]

To a solution of the complex $[PtCl\{P(O)Ph_2\}\{P(OH)Ph_2\}_2]$ (400 mg; 0.48 mmol) in benzene (30 cm^3), a stoichiometric amount of the corresponding salt Ag(S—S) (0.48 mmol) [S_2CNEt_2: 122 mg; $S_2P(OEt)_2$: 140 mg] was added. The resulting mixture was boiled under reflux for 18 h. The silver chloride formed was filtered off through Kieselguhr, and the filtrate was concentrated under reduced pressure to a small volume. The complexes, precipitated as white solids by addition of n-hexane, were washed with n-hexane, dried *in vacuo* and crystallized from dichloromethane–n-hexane. Compound **1**: yield 279 mg (78%). Found: C, 47.2; H, 4.2. Calc. for $C_{29}H_{31}O_2NP_2S_2Pt$: C, 46.7; H, 4.1%. Compound **2**: yield 285 mg (76%). Found: C, 43.3; H, 3.7. Calc. for $C_{28}H_{31}O_4P_3S_2Pt$: C, 42.9; H, 3.9%.

Preparation of $[Pt(S_2COEt)\{P(O)Ph_2\}\{P(OH)Ph_2\}]$ (**3**)

To a solution of the complex $[PtCl\{P(O)Ph_2\}\{P(OH)Ph_2\}_2]$ (300 mg; 0.36 mmol) in a benzene–methanol–chloroform mixture (30:15:5 cm^3), a stoichiometric amount of TlS_2COEt (117 mg; 0.36 mmol) was added. The heterogeneous mixture was boiled under reflux for 14 h. The mixture was filtered through cellulose to remove the TlCl formed and the yellow solution obtained was chromatographed on Kieselgel (HF_{254}, type 60) using dichloromethane as eluent. The solution obtained was concentrated under reduced pressure to a small volume and the complex precipitated by addition of n-hexane. The white solid obtained was washed with n-hexane and diethylether, dried *in vacuo*, and crystallized from chloroform–n-hexane. Yield 180 mg (70%). Found: C, 44.8; H, 4.0. Calc. for $C_{27}H_{26}O_3P_2S_2Pt$: C, 45.1; H, 3.6%.

Preparation of $[Pt\{S_2P(O)(OEt)\}\{P(O)Ph_2\}\{P(OH)Ph_2\}]Na$ (**4**)

A mixture of complex **2** (70 mg; 0.089 mmol) and a large excess of NaI (20 mg; 0.13 mmol) in acetone (20 cm^3) was boiled under reflux for 4 h. The solution obtained was evaporated to dryness and the product extracted from the residue with chloroform. The excess of NaI was filtered off through Kieselguhr and the solution was concentrated under reduced pressure to a small volume. Addition of diethyl ether gave a yellow precipitate, which was filtered, washed with diethyl ether and dried *in vacuo*. Yield 49 mg (70%). Found: C, 39.7; H, 3.7. Calc. for $C_{26}H_{26}O_4P_3S_2PtNa$: C, 40.2; H, 3.3%. $\Lambda_M = 62\ cm^2\ mol^{-1}\ \Omega^{-1}$.

Preparation of $[Pt\{S_2CO\}\{P(O)Ph_2\}\{P(OH)Ph_2\}]Na$ (**5**)

This compound was prepared analogously as described for **4** starting from **3** (70 mg; 0.097 mmol) and NaI (22 mg; 0.15 mmol). A white solid was obtained by addition of n-hexane. Yield 37 mg (53%). Found: C, 42.2; H, 3.4. Calc. for $C_{25}H_{21}O_3P_2S_2PtNa$: C, 42.1; H, 3.0%.

Preparation of $[Pt\{S_2P(O)(OEt)\}\{P(O)Ph_2\}\{P(OH)Ph_2\}]PPh_4$ (**6**)

A solution of complex **4** (40 mg; 0.052 mmol) in acetone (20 cm^3) was treated with Ph_4PBr (22 mg; 0.052 mmol). The solution was boiled under reflux for 3 h. The mixture obtained was evaporated to dryness and the residue was dissolved in acetone. The NaBr formed was filtered off through Kieselguhr and the solution was concentrated under reduced pressure to a small volume. Addition of diethyl ether gave a yellow precipitate, which was filtered, washed with diethyl ether and dried *in vacuo*. Yield 42 mg (75%). Found: C, 54.6; H, 4.4. Calc. for $C_{50}H_{46}O_4P_4S_2Pt$: C, 54.9; H, 4.2%. $\Lambda_M = 84\ cm^2\ mol^{-1}\ \Omega^{-1}$. IR (KBr): $\nu(PO) = 1095\ cm^{-1}$.

Preparation of $[Pt(S_2CO)\{P(O)Ph_2\}\{P(OH)Ph_2\}]PPh_4$ (**7**)

Ph_4PBr (24 mg; 0.056 mmol) was added to a solution of complex **5** (40 mg; 0.056 mmol) in acetone (20 cm^3). The solution was boiled under reflux for 3 h and the mixture obtained was evaporated to dryness. The solid residue was extracted with chloroform, filtered and the solution concentrated under reduced pressure to a small volume. Addition of diethyl ether gave a yellow precipitate, which was filtered, washed with diethyl ether and dried *in vacuo*. Yield 37 mg (64%). Found: C, 57.4; H, 4.4. Calc. for $C_{49}H_{41}O_3P_3S_2Pt$: C, 57.2; H, 4.0%.

Preparation of $[Pt\{S_2COEt\}\{P(OMe)Ph_2\}_2]Cl$ (**8**)

To a solution of the complex $[Pt(S_2COEt)_2]$ (60 mg; 0.14 mmol) in dichloromethane (20 cm^3), an excess of the ligand $P(OMe)Ph_2$ (0.3 cm^3; 1.5 mmol) was added. After stirring the solution at room temperature for 20 min, the solution was evaporated to dryness and the product extracted from the residue with diethyl ether. The solution obtained was filtered off through cellulose and concentrated under reduced pressure to a small volume. Addition of n-hexane gave a white precipitate, which was filtered, washed with n-hexane and dried *in vacuo*. Crystallization at −20°C from diethyl ether–n-hexane gave colourless crystals. Yield 116 mg (54%). Found: C, 44.7; H, 4.1. Calc. for $C_{29}H_{31}O_3P_2S_2ClPt$: C, 44.4; H, 4.0%. IR (KBr): $\nu(PO) = 1030\ cm^{-1}$.

Preparation of $[Pt\{S_2CO\}\{P(OMe)Ph_2\}_2]$ (**9**)

This complex could be prepared by the two methods described below.

(a) To a solution of complex **8** (100 mg; 0.13 mmol) in a dichloromethane–acetone (1 : 1) mixture, an excess of NaI (30 mg; 0.2 mmol) was added. After stirring the solution at room temperature for 24 h, the solution obtained was evaporated to dryness and the product extracted from the residue with chloroform. The excess of NaI was filtered off through Kieselguhr and the solution concentrated under reduced pressure to a small volume. Addition of n-hexane or diethyl ether gave a white precipitate, which was filtered, washed with n-hexane and dried *in vacuo*. Crystallization at −20°C from dichloromethane–diethyl ether gave colourless crystals. Yield 76 mg (83%).

(b) To a solution of the complex $[Pt\{S_2COEt\}_2]$ (120 mg; 0.27 mmol) in dichloromethane (20 cm^3) an excess of $P(OMe)Ph_2$ (0.2 cm^3; 0.98 mmol) was added. The solution was boiled under reflux for 3 h and then concentrated to a small volume. Addition of n-hexane or diethyl ether gave a white precipitate, which was filtered off, washed with n-hexane and dried *in vacuo*. Crystallization at −20°C from dichloromethane–diethyl ether gave colourless crystals. Yield 104 mg (53%). Found: C, 45.3; H, 3.9. Calc. for $C_{27}H_{26}O_3P_2S_2Pt$: C, 45.1; H, 3.6%. IR (KBr): $\nu(CO) = 1680$, 1605 and 1580 cm^{-1}; $\nu(PO) = 1095\ cm^{-1}$.

Preparation of $[Pt\{S_2P(O)(OEt)\}\{P(OMe)Ph_2\}_2]$ (**10**)

A solution of the complex $[Pt\{S_2P(OEt)_2\}_2]$ (100 mg; 0.18 mmol) and an excess of $P(OMe)Ph_2$ (0.2 cm^3; 0.98 mmol) in dichloromethane (20 cm^3) was boiled under reflux for 3 h. The solution formed was concentrated to a small volume and the addition of n-hexane or diethyl ether gave a yellow precipitate, which was filtered off, washed with n-hexane and dried *in vacuo*. Yield 102 mg (74%). Found: C, 43.0; H, 4.0. Calc. for $C_{28}H_{31}O_4P_3S_2Pt$: C, 42.9; H, 4.0%.

Crystal structure of complex **9**

A colourless, prismatic-shaped single crystal of average dimensions $0.52 \times 0.52 \times 0.76$ mm, obtained from slow diffusion of n-hexane into a dichloromethane solution of the complex, was selected for structure determination by X-ray diffraction. Intensity data were collected on a Siemens R3m/V four-circle diffractometer, using a θ–2θ scan technique and graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Two standard reflections, monitored every 98 reflections, showed no significant intensity variations during data collection. A total of 6609 reflections was collected for structure analysis with $2.5 \leqslant 2\theta \leqslant 54.0°$ ($0 \leqslant h \leqslant 13$, $0 \leqslant k \leqslant 19$, $-22 \leqslant l \leqslant 22$) and merged to give 6063 independent reflections ($R_{\text{int}} = 0.027$), of which 5604 reflections with $F > 2\sigma(F)$ were considered observed. Corrections were applied for Lorentz and polarization effects; semi-empirical corrections for absorption were applied with maximum and minimum transmission factors of 0.1075 and 0.0584, respectively.

A summary of the crystal data is presented in Table 1. The structure was solved by direct methods and refined on F by full-matrix least-squares calculations. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at geometrically idealized positions with C—H = 0.96 Å and were allowed to ride over their parent carbon atoms with their corresponding equivalent isotropic displacement parameters. The total number of parameters refined was 317. Final R and R_w values were 0.0286 and 0.0270, respectively [weighting scheme $w^{-1} = \sigma^2(F) + 0.0007F^2$], and goodness-of-fit $S =$ 1.01. Largest and mean shift/error of final cycle of refinement were 0.007 and 0.001, respectively. All calculations were performed with the Siemens SHELXTL PLUS system.[12] The absolute structure was determined using the SHELXTL routine to refine the Rogers η parameter, which converged to $+1.065(13)$.[13] Full lists of bond distances and bond angles, anisotropic thermal parameters, hydrogen-atom parameters, relevant planes and dihedral angles, and observed and calculated structural factors have been deposited with the Editor as supplementary material.

Table 1. Crystal data for $[Pt(S_2CO)\{P(OMe)Ph_2\}_2]$

Empirical formula	$C_{27}H_{26}O_3P_2PtS_2$
Crystal system	orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	
a (Å)	10.416(2)
b (Å)	14.913(4)
c (Å)	17.861(4)
Volume (Å^3)	2774.3(12)
Z	4
Formula weight (g mol^{-1})	719.6
Density (calc.) (Mg m^{-3})	1.723
Absorption coefficient (mm^{-1})	5.350
$F(000)$	1408

RESULTS AND DISCUSSION

It has been shown previously that the complex $[Pt(S_2CNEt_2)_2]$ reacts slowly with Ph_2POMe in dichloromethane solution to produce the neutral compound $[Pt\{S_2CNEt_2\}\{P(O)Ph_2\}\{P(OH)Ph_2\}]$[7] (**1**). In the course of our investigations on platinum(II)–phosphinite complexes, we found that the complex $[PtCl\{P(O)Ph_2\}\{P(OH)Ph_2\}_2]$ reacted easily in organic solvents with stoichiometric amounts of silver or thallium(I) salts of dithiolate ligands to yield the corresponding neutral complexes $[Pt(S—S)\{P(O)Ph_2\}\{(P(OH)Ph_2\}]$ in high yields (>70%), where $(S—S)^- = (S_2CNEt_2)^-$ (**1**), $\{S_2P(OEt)_2\}^-$ (**2**) and $(S_2COEt)^-$ (**3**).

The reaction of neutral complexes **2** and **3** in acetone solution with a large excess of NaI involves the evolution of EtI and the formation of the sodium salts of the anionic complexes $[Pt\{S_2P(O)(OEt)\}\{P(O)Ph_2\}\{P(OH)Ph_2\}]Na$ (**4**) and $[Pt\{S_2CO\}\{P(O)Ph_2\}\{P(OH)Ph_2\}]Na$ (**5**), respectively. The treatment of complexes **4** and **5** with Ph_4PBr in acetone solution at reflux temperature produces the methathetic exchange of the sodium cation with precipitation of NaBr, and formation of the corresponding complexes $[Pt\{S_2P(O)(OEt)\}\{P(O)Ph_2\}\{P(OH)Ph_2\}]PPh_4$ (**6**) and $[Pt\{S_2CO\}\{P(O)Ph_2\}\{P(OH)Ph_2\}]PPh_4$ (**7**), respectively.

All new compounds were isolated as stable solids and characterized by means of elemental analyses and spectroscopic techniques. Their solid-state IR spectra, in KBr pellets, show the presence of characteristic absorptions of ν(PO) in the 1050–1005 cm^{-1} range, and for complexes **5** and **7**, the three corresponding stretching frequencies assigned to the ketonic group of the dithiocarbonate ligand at 1678, 1610, 1585 cm^{-1} and 1680, 1610, 1580 cm^{-1}, respectively.[10]

The ^1H NMR spectra of these complexes (**1**–**4**, **6**) exhibit characteristic resonances of the ethyl groups of the dithiolate ligands, as a triplet and as a quartet for the methyl and methylene protons, in the ranges δ 1.10–1.43 and 3.57–4.59 ppm, respectively. For compounds **2**, **4** and **6** the methylene protons appear as a doublet of quartets due to a coupling with the phosphorus atom (P_B) of the mono- or diethyldithiophosphate ligand. Relevant

Table 2. NMR chemical shifts (δ, ppm) and coupling constants (Hz) of platinum(II) complexes[a]

	^{1}H				$^{31}P\{^{1}H\}$	
Complex	$\delta(CH_3)$	$\delta(CH_2)$	$^{3}J_{H-H}$	$\delta(OCH_3)$	$\delta(P)$	$^{1}J_{Pt-P}$
1	1.21 (t)	3.57 (c)	7.16	—	60.57 (s)	3511
2[b]	1.30 (t)	4.06 (c)	7.09	—	57.70 (d, P_A)	3739
		4.08 (c)			96.77 (t, P_B)	225 (^{2}J)
3	1.43 (t)	4.59 (c)	7.15	—	58.28 (s)	3504
4[c]	1.26 (t)	3.80 (m)	7.12	—	60.48 (d, P_A)	3641
					75.87 (t, P_B)	220 (^{2}J)
5	—	—	—	—	54.98 (s)	3802
6[d]	1.10 (t)	3.83 (c)	7.05	—	62.85 (d, P_A)	3592
		3.82 (c)			68.34 (t, P_B)	218 (^{2}J)
7[e]	—	—	—	—	57.50 (s)	3912
8[f]	1.21 (t)	4.11 (c)	7.03	3.62 (d)	95.47 (s)	3482
9[g]	—	—	—	3.48 (d)	97.63 (s)	3576
10[h]	1.23 (t)	3.88 (c)	7.05	3.44 (d)	94.58 (d, P_A)	3765
		3.92 (c)			62.27 (t, P_B)	253 (^{2}J)

[a] Measured in $CDCl_3$ at room temperature. Chemical shifts relative to Me_4Si and H_3PO_4 (85%) as standards. s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. All complexes show multiplets in the region: δ 7.1–8.0 ppm.

[b] $^{3}J_{P_B-H} = 9.7$ Hz, $^{3}J_{P_A-P_B} = 4.0$ Hz.

[c] $^{3}J_{P_A-P_B} = 4.2$ Hz.

[d] $J_{P_B-H} = 2.1$ Hz; $^{31}P\{^{1}H\}$ NMR: $\delta(Ph_4P) = 22.15$ ppm (s).

[e] $^{31}P\{^{1}H\}$ NMR: $\delta(Ph_4P) = 22.30$ ppm (s).

[f] $^{3}J_{P-H} = 12.3$ Hz.

[g] $^{3}J_{P-H} = 12.5$ Hz; $^{13}C\{^{1}H\}$ NMR: $\delta(CO) = 192.8$ ppm (s).

[h] $J_{P_B-H} = 2.4$ Hz, $^{3}J_{P_A-P_B} = 4.8$ Hz.

NMR chemical shifts and coupling constants are listed in Table 2.

The nucleophilic attack on an alkoxy group of the coordinated dithiolate ligand of complex **2**, by I^- in deuteriated acetone at 20°C, was performed initially in an NMR tube. Figure 1 shows the slow formation of the anionic complex **4** by the merging of the triplet and multiplet resonances centred at δ 1.45 and 4.15 ppm, assigned to the ethyl group. These signals are shifted to high field compared to resonances of the starting complex [δ 1.7 (t) and 4.53 (dq)] due to the increase of the electron density on the phosphorus atom and, consequently, on the remaining ethyl group. The triplet and quartet resonances appear at δ 2.15 and 3.60 ppm, respectively, indicating the formation of EtI.

The high resolution $^{31}P\{^{1}H\}$ NMR spectra show a singlet for complexes **1**, **3**, **5** and **7**, and a doublet resonance for complexes **2**, **4** and **6**, in the δ 57–61 ppm range, corresponding to the phosphorus atoms (P_A) of the phosphinite and phosphinous acid groups. These results indicate that both phosphorus atoms are equivalent due to the symmetrical metallocycle formed $[(S—S)Pt\{\eta^{2}Ph_2PO\cdots H\cdots OPPh_2—P,P\}]^{0,1-}$. The complexes which contain the ligand ethyldithiophosphate show, moreover, a triplet signal assigned to the resonance of the phosphorus atom (P_B) of the ligand. As expected, the phosphorus atoms P_A and P_B present a coupling with the platinum atom, $^{1}J_{Pt-P_A}$ and $^{2}J_{Pt-P_B}$, respectively.[14,15] Interestingly, the comparison of the spectra of the starting complex **2** with that of the corresponding anionic derivative **4** shows that the resonances assigned to the P_A atoms for complex **4** shift slightly to low field, along with a decrease in the coupling constant $^{1}J_{Pt-P_A}$. The resonance assigned to the P_B atom of the ethyldithiophosphate ligand is shifted to high field, with a small decrease in the coupling constant $^{2}J_{Pt-P_B}$ (Table 2). Similar chemical shift displacements were observed in the transformation of the coordinated ethyldithiocarbonate ligand **3** into a dithiocarbonate group **5**. These results indicate that the $\{S_2P(O)(OEt)\}^{2-}$ and $\{S_2CO\}^{2-}$ groups are stronger ligands than the $\{S_2P(OEt)_2\}^{-}$ and $\{S_2COEt\}^{-}$ groups, respectively, in agreement with those reported by Colton for related dithiolate complexes.[16]

Unfortunately, all attempts to prepare suitable crystals of the anionic complexes to carry out X-

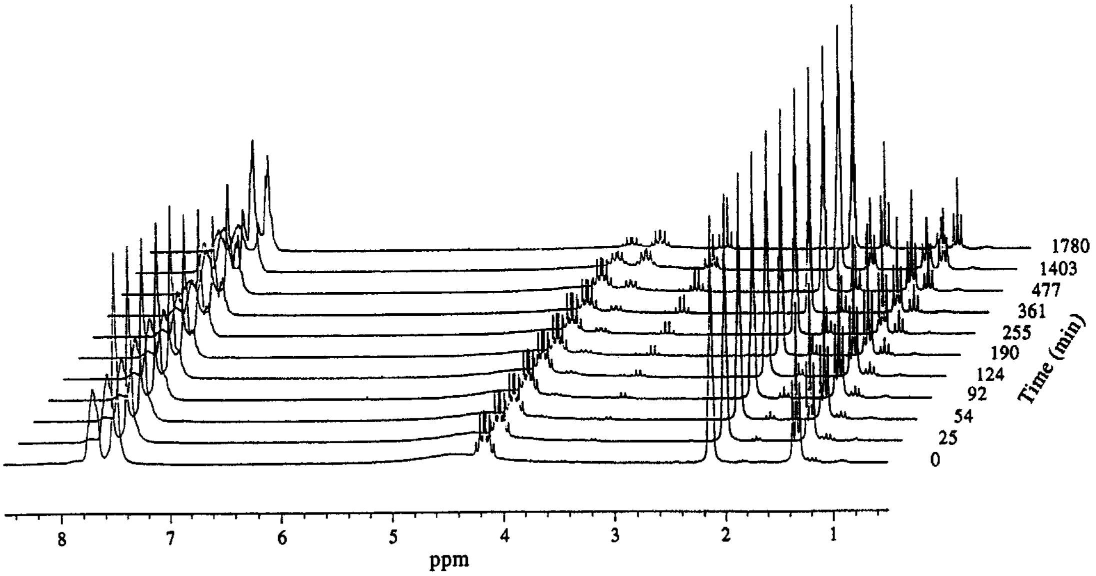

Fig. 1. Time evolution of the ^1H NMR spectrum of complex **2** in the presence of NaI in deuterated acetone at 20°C.

ray characterization have so far been unsuccessful. For this reason and to support the NMR assignments, we prepared a family of similar dithiolate complexes containing methyldiphenylphosphinite as ligand. Thus, the complex $[Pt(S_2COEt)_2]$ reacts in dichloromethane with $P(OMe)Ph_2$ in a 1 : 2 molar ratio, with displacement of one dithiolate ligand molecule, to form a cationic complex which was isolated as a chloride compound due to the decomposition of the solvent, $[Pt(S_2COEt)\{P(OMe)Ph_2\}_2]Cl$ (**8**). This complex reacts with an excess of NaI with evolution of EtI and formation of the neutral complex $[Pt(S_2CO)\{P(OMe)Ph_2\}_2]$ (**9**). These two steps are produced simultaneously in a similar reaction of complex $[Pt\{S_2P(OEt)_2\}_2]$ with $P(OMe)Ph_2$ in dichloromethane at reflux temperature, to give the neutral complex $[Pt\{S_2P(O)(OEt)\}\{P(OMe)Ph_2\}_2]$ (**10**).

The solid-state IR spectra of complexes **8**–**10** show the $\nu(PO)$ absorption in the 1050–1005 cm^{-1} range, and complex **9** shows the corresponding $\nu(CO)$ frequencies at 1680, 1605 and 1580 cm^{-1}. Their ^1H NMR spectra exhibit a doublet resonance for the methoxy protons of the $P(OMe)Ph_2$ ligand, with $^3J_{PH}$ coupling in the range 12–13 Hz and triplet and quartet resonances assigned to the ethoxy group of the dithiolate ligand in complexes **8** and **10**. The $^{31}P\{^1H\}$ NMR spectra of complexes **8** and **9** show a singlet resonance at δ 95.5 ($^1J_{Pt\text{-}P_A}$ = 3482 Hz) and 97.6 ppm ($^1J_{Pt\text{-}P_A}$ = 3576 Hz), respectively, assigned to the equivalent $P(OMe)Ph_2$ ligands. Complex **10** exhibits a doublet resonance at δ 94.58 ppm ($^1J_{Pt\text{-}P_A}$ = 3765 Hz) for the equivalent phosphorus atoms of the Ph_2POMe ligands and a triplet signal at δ 62.27 ppm ($^1J_{Pt\text{-}P_B}$ = 253 Hz, $^3J_{P_A\text{-}P_B}$ = 4.8 Hz), assigned to the resonance of the phosphorus atom of the ethyldithiophosphinite ligand. The coupling constant $^1J_{Pt\text{-}P_A}$ of complex **9** is smaller than that of complex **10**, indicating that the *trans* influence of the $\{S_2CO\}^{2-}$ group is larger than that of $\{S_2P(O)(OEt)\}^{2-}$ and, consequently, the thiocarbonate group is a stronger ligand than the ethyldithiophosphate group.[17]

Crystal structure of $[Pt(S_2CO)\{P(OMe)Ph_2\}_2]$

Relevant bonds distances and angles are given in Table 3. Figure 2 shows a molecular representation of the neutral complex, in which the platinum atom is coordinated to the phosphorus atoms of the two phosphine ligands in *cis* positions and a bidentate sulphur-bonded dithiocarbonate ligand, acquiring a square-planar environment (mean dev. = 0.008 Å).

The Pt—P and Pt—S bond lengths [average: 2.255(2) and 2.334(2) Å, respectively] are similar to those in the closely related complex $[Pt(S_2CO)(PPh_3)_2]$ [Pt—P, av. 2.284(4) Å and Pt—S, av. 2.336(3) Å].[18] The C—S [1.765(7) and 1.767(7) Å] and C—O [1.190(8) Å] distances of the coordinated dithiocarbonate ligand are similar to those found in the related complexes $[Pt(S_2CO)(PPh_3)_2]$[18] [C—S: average 1.779(15) Å; C—O: 1.195(16) Å] and $[Pd(S_2CO)(PMe_2Ph)_2]$[19] [C—S: average 1.769(9) Å; C—O: 1.230(2) Å]. Interestingly, the C—O dis-

Table 3. Selected bond distances (Å) and bonds angles (°), with e.s.d.s in parentheses

Pt—S(1)	2.333(2)	P(1)—O(1)	1.600(5)
Pt—S(2)	2.336(2)	P(1)—C(111)	1.826(6)
Pt—P(1)	2.250(2)	P(1)—C(121)	1.815(6)
Pt—P(2)	2.261(2)	P(2)—O(2)	1.601(5)
S(1)—C(1)	1.767(7)	P(2)—C(211)	1.801(7)
S(2)—C(1)	1.765(7)	P(2)—C(211)	1.807(6)
O(1)—C(1)	1.190(8)		

S(1)—Pt—S(2)	75.2(1)	S(1)—Pt—P(1)	169.3(1)
S(2)—Pt—P(1)	94.2(1)	S(1)—Pt—P(2)	93.5(1)
S(2)—Pt—P(2)	168.6(1)	P(1)—Pt—P(2)	97.2(1)
Pt—S(1)—C(1)	88.7(2)	Pt—S(2)—C(1)	88.6(2)
Pt—P(1)—O(1)	109.8(2)	Pt—P(1)—C(111)	116.0(2)
O(1)—P(1)—C(111)	105.2(3)	Pt—P(1)—C(121)	114.7(2)
O(1)—P(1)—C(121)	106.6(3)	C(111)—P(1)—C(121)	103.7(3)
Pt—P(2)—O(2)	117.6(2)	Pt—P(2)—C(211)	116.1(2)
O(2)—P(2)—C(211)	105.7(3)	Pt—P(2)—C(221)	112.0(2)
O(2)—P(2)—C(221)	98.4(3)	C(211)—P(2)—C(221)	104.9(3)
S(1)—C(1)—S(2)	107.5(3)	S(1)—C(1)—O(1)	126.5(6)
S(2)—C(1)—O(1)	126.0(6)		

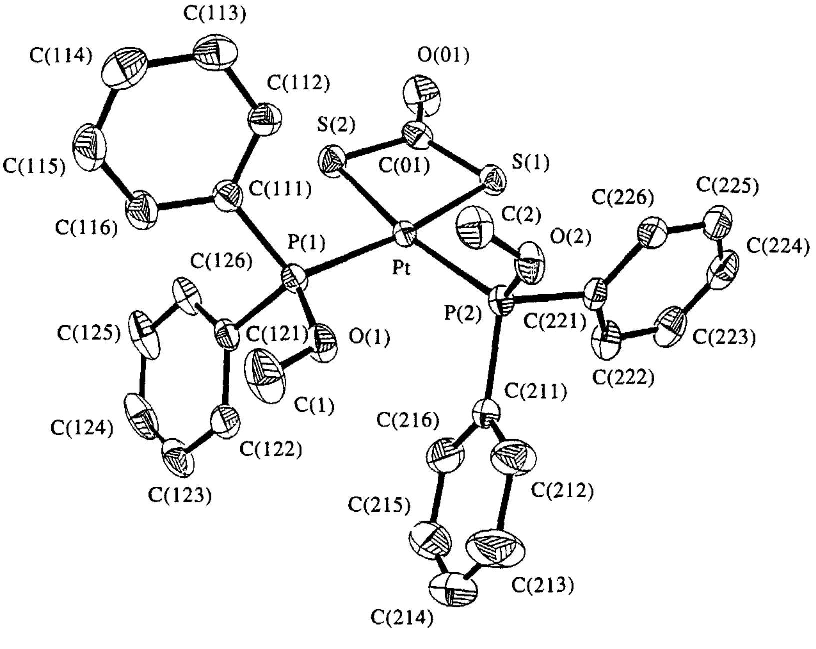

Fig. 2. ORTEP view of the structure of the complex $[\mathrm{Pt}\{\mathrm{S_2CO}\}\{\mathrm{P(OMe)Ph_2}\}_2]$ showing the atom numbering. Hydrogen atoms have been omitted for clarity.

tance is shorter than the ketonic C═O bonds, probably due to the π-electronic effects of the phosphine ligands, in *trans* positions to the sulphur atoms in the bidentate ligand.

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