

Synthesis and crystal structure of a diplatinum cyclopentadienyldiphenylphosphine sulphide bridged complex

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Abstract

The mixed early–late Ti–Pt₂ compound $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Ti}(\mu_3\text{-}1\eta^5\text{-C}_5\text{H}_4\text{P}(\text{S})\text{Ph}_2\text{-}2,3\kappa\text{S})(\mu\text{-SPh})_2\{\text{Pt}(\text{C}_6\text{F}_5)_2\}_2]$ (**3**) containing a functionalised thiophosphorylcyclopentadienyl $\text{S}=\text{PPh}_2\text{C}_5\text{H}_4$ bridging ligand has been obtained by reaction of $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)(\eta^5\text{-C}_5\text{H}_4\text{P}(\text{S})\text{Ph}_2)\text{Ti}(\text{SPh})_2]$ (**1**) with 2 equivalents of $\text{cis-}[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{thf})_2]$. The crystallisation of **3** in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ at -20°C gave the unexpected diplatinum complex $[\text{Pt}(\text{C}_6\text{F}_5)_2(\mu\text{-SPPH}_2\text{C}_5\text{H}_5)]_2$ (**4**) with an unusual double bis-cyclopentadienyldiphosphine sulphide bridging system ($\mu\text{-}\kappa\text{S}$), which has been characterised by X-ray diffraction. As an alternative route to the synthesis of **4** the reaction of $\text{cis-}[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{thf})_2]$ with $\text{S}=\text{PPh}_2\text{C}_5\text{H}_5$ has been studied. Independently of the stoichiometry employed, this reaction gives mixtures of **4** and the novel mononuclear complex $\text{cis-}[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{S}=\text{PPh}_2\text{C}_5\text{H}_5)]$ (**6**). Low temperature control of this reaction indicates that both complexes (**4** and **6**) are formed through a common intermediate identified as $\text{cis-}[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{S}=\text{PPh}_2\text{C}_5\text{H}_5)(\text{thf})]$ (**5**) on the basis of spectroscopic techniques. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cyclopentadienyldiphenylphosphine sulphide; Bridging; Diplatinum; Trimetallic TiPt₂ complex

1. Introduction

The coordination chemistry of thiophosphoranyl ($\text{S}=\text{PR}_3$) ligands has been of great interest over these last decades [1]. This attention derives not only from spectroscopic and structural aspects, which have played an important role in the development of a model for the phosphoryl bond, but also from their chemical behaviour and particularly their catalytic activity [1,2]. Polyfunctional bis- and tris(chalcogenide)phosphoranyl ligands and hybrid ligands containing also different donor atoms have been a subject of growing interest lately due to their versatile coordination behaviour [3].

Tertiaryphosphine sulphides have been used extensively as terminal ligands both as sulphur σ -bonded

[1,4] and as π donors employing P–S π bonding electrons for donation [1b]. Complexes containing $\text{S}=\text{P}(\text{R}/\text{R}')_3$ bridging ligands have been also prepared [4i,5] but as far as we know only two examples have been structurally characterised [5c,d]. Such $\mu\text{-}\kappa\text{S}$ bonding mode of a thiophosphoranyl ($\text{S}=\text{PR}_2$) function has been also found to be present in a few silver [6] and copper [7] complexes obtained by coordination of polydentate or dithio phosphoranyl ligands; Forniés et al. have also reported the preparation of Pd₃ and Pd₂Pt complexes containing a related triply-bridging diphenylthiophosphinito ($\mu_3\text{-}\kappa\text{P}:\kappa^2\text{S}\text{-SPPH}_2$) ligand [8].

In this paper we describe the formation of a diplatinum complex $[\text{Pt}(\text{C}_6\text{F}_5)_2(\mu\text{-SPPH}_2\text{C}_5\text{H}_5)]_2$ with an unusual double bis-(cyclopentadienyldiphenylphosphine sulphide) bridging system. Crystals of this complex were unexpectedly formed by slow crystallisation of a mixed early–late Ti–Pt₂ compound containing a functionalised thiophosphorylcyclopentadienyl $\text{S}=\text{PPh}_2\text{-C}_5\text{H}_4^-$ anion as bridging ligand. In this context,

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it is rather surprising that since Mathey and Lampin published the synthesis [9a] of S=PPh₂C₅H₅ and its behaviour towards iron and manganese carbonyls [9b], coordination chemistry of this ligand with transition metals remains almost unexplored. Therefore, and seeking an alternative route to **4**, the reactivity of *cis*-[Pt(C₆F₅)₂(thf)₂] towards S=PPh₂C₅H₅ has also been explored.

2. Experimental

All preparative reactions and manipulations were carried out under argon atmosphere using standard Schlenk techniques [10]. Solvents were purified according to standard methods [11]. The starting materials *cis*-[Pt(C₆F₅)₂(thf)₂] [12], [(η⁵-C₅H₄SiMe₃)(η⁵-C₅H₄P(S)Ph₂)Ti(SPh)₂] [13] and S=PPh₂C₅H₅ [9a] were obtained as previously described. ¹H, ³¹P{¹H} and ¹⁹F NMR were registered on Bruker ARX-300 and AMX-300 spectrometers and chemical shifts (ppm) were reported relative to external standards (SiMe₄, CFC₃ and 85% H₃PO₄). IR spectra were recorded on Perkin Elmer 1650 FTIR and Perkin Elmer 883 spectrophotometers. The mass spectra (FAB⁺) were carried out on a VG Autospec Spectrometer and elemental analyses were performed on Perkin-Elmer 240-B and Perkin-Elmer 2400 CHNS/O microanalyzers.

2.1. Preparation of [(η⁵-C₅H₄SiMe₃)Ti(μ₃-1η⁵-C₅H₄P(S)Ph₂-2,3κS)(μ-SPh)₂{Pt(C₆F₅)₂}₂] (**3**)

To a CH₂Cl₂ (15 ml) solution of [(η⁵-C₅H₄SiMe₃)(η⁵-C₅H₄P(S)Ph₂)Ti(SPh)₂] **1** (0.10 g, 0.15 mmol) was added *cis*-[Pt(C₆F₅)₂(thf)₂] (0.20 g, 0.30 mmol). The mixture was stirred under argon for 30 min while a progressive colour change from green to red was observed. Subsequently, the resulting solution was evaporated to dryness. The residue was treated with 4 ml of toluene and kept at -20°C overnight giving **3** as a microcrystalline red solid (0.22 g, 83% yield). Anal. Calc. for C₆₁H₃₇F₂₀PPt₂S₃SiTi (1743.24): C, 42.03; H, 2.14; S, 5.52. Found: C, 42.25; H, 2.17; S, 5.14%. ¹H NMR (CDCl₃): δ (ppm) 9.15 (br, C₆H₅), 8.36–8.23, 7.97–7.15 (m, C₆H₅), 6.50 (2H), 6.34 (1H), 6.16 (1H), 5.95 (2H), 5.54 (1H), 4.39 (1H) (C₅H₄), -0.09 (9H, Si(CH₃)₃). ³¹P{¹H} NMR (CDCl₃): δ (ppm) 28.2 (s, ²J(Pt–P) ~ 60 Hz). ¹⁹F NMR (CDCl₃): δ (ppm) -114.24 (*J*(Pt–F_o) = 413 Hz), -116.48, -117.87, -118.03 (d), -118.34, -119.29, -119.88; -120.80 (m, 8F_o); -159.30 (t), -160.27 (t), -161.8 (t), -162.5 (t) (4F_p); -163.29 (2F), -163.72 (3F), -164.26 (1F), -164.78 (1F), -165.20 (1F). IR (cm⁻¹) (Nujol): ν 803 (s, br) (X-sens C₆F₅); 636 (m) (P=S). Mass spectrum (FAB⁺): *m/z* (%): 1575 (0.2) [(M–C₆F₅)⁺], 1405 (0.03) [(M–2C₆F₅–3H)⁺], 1214 (0.03) [(M–Pt(C₆F₅)₂)⁺], 1103

(2) [(M–Pt(C₆F₅)₂–SPh–H)⁺], 1047 (0.2) [(M–Pt(C₆F₅)₃)⁺], 936 (0.2) [(M–Pt(C₆F₅)₃–SPh–H)⁺], 575 (12) [(Ti(SPh)(C₅H₄SiMe₃)(C₅H₄P(S)Ph₂)⁺], 466 (22) [(Ti(C₅H₄SiMe₃)(C₅H₄P(S)Ph₂)⁺], 307 (40) [(Ti(C₅-H₄SiMe₃)(C₅H₄P(S)Ph₂)–C₅H₄Me₂PS–2H)⁺], 154 (100) [(Ti(C₅H₄SiMe–H)⁺].

2.2. Preparation of [Pt(C₆F₅)₂(μ-SPPPh₂C₅H₅)₂] (**4**)

A slow diffusion of MeOH into a CH₂Cl₂ (1:1) solution of **3** at -20°C gave pale orange crystals of compound **4** in low yield.

2.3. Reaction of *cis*-[Pt(C₆F₅)₂(thf)₂] with S=PPh₂C₅H₅

2.3.1. 1:1 molar ratio

To a solution of *cis*-[Pt(C₆F₅)₂(thf)₂] (0.150 g, 0.223 mmol) in CH₂Cl₂ (10 ml) was added S=PPh₂C₅H₅ (0.063 g, 0.223 mmol), giving a pale-orange solution immediately. In a few seconds, a white-cream solid began to precipitate (0.033 g) which, after filtration, was identified as a mixture of **4** and **6** (proportion based on ³¹P **4/6** 1:3.7). The resulting solution was immediately evaporated to dryness and the ³¹P NMR spectrum of this cream solid residue showed it to be a mixture of **4** and **6** among other unidentified species (proportion **4/6** 1:1.45).

When a fresh solution of S=PPh₂C₅H₅ (0.042 g, 0.148 mmol) in CH₂Cl₂ (2 ml) was added dropwise to a solution of *cis*-[Pt(C₆F₅)₂(thf)₂] (0.1 g, 0.148 mmol) in CH₂Cl₂ (2 ml) at 0°C, a pale-orange solution was formed and in a few seconds a white suspension was produced. After 5 min at 0°C, the solid was filtered off and identified (³¹P NMR) as **4** (0.03 g, 13% yield). Evaporation of the filtrate to dryness gave a solid residue, which was identified mainly as **4**.

2.3.2. 1:2 molar ratio

A solution of *cis*-[Pt(C₆F₅)₂(thf)₂] (0.0596 g, 0.088 mmol) in CH₂Cl₂ (5 ml) was treated at room temperature (r.t.) with S=PPh₂C₅H₅ (0.05 g, 0.177 mmol) (molar ratio 1:2). After a few seconds, a white precipitate formed. The mixture was stirred for 15 min and then the solid was filtered off (0.02 g) and identified as a mixture of **4** and **6** (proportion **4/6** 1:1.6). The filtrate was evaporated to dryness and treated with *n*-hexane (3 ml) giving **6** as a white-cream solid (0.062 g, 65% yield).

2.4. NMR monitored reaction

2.4.1. 1:1 molar ratio

A mixture of *cis*-[Pt(C₆F₅)₂(thf)₂] (0.03 g, 0.0445 mmol) and S=PPh₂C₅H₅ (0.0126 g, 0.0445 mmol) was dissolved in 0.6 ml of CDCl₃ at -50°C and the reac

tion was immediately monitored by NMR spectroscopy. Integration of the NMR signals at this temperature showed an approximate 2.6:1 proportion of the complexes **5** and **6**. When the temperature was increased to -10°C a new signal corresponding to the compound **4** (10:6.6:1 **5/6/4**) began to appear. At 20°C , the signal due to the derivative **5** disappeared and only the species **4** and **6** were detected in a final ratio (1:5 **4/6**). After 1 hr. at this temperature, the intensity of the signal due to the derivative **5** decreased while the signal attributed to **4** increased with the final proportion being **4/6** 1.1:1.

2.4.2. 1:0.5 molar ratio

cis-[Pt(C₆F₅)₂(thf)₂] (0.03 g, 0.0445 mmol) was added to a solution of S=PPh₂C₅H₅ (0.0063 g, 0.0225 mmol) in CDCl₃ (0.6 ml) at -50°C , and a ³¹P NMR spectrum was taken immediately, revealing the presence of complex **5** as the main component together with **4** and **6** (proportion \sim 21:9:1 **5/6/4**) among other signals. When the temperature was increased slowly, the signal of the complex **4** was increasing and at r.t. only the signal of this complex was observed. **4** can be isolated pure in this reaction and it is identified as [Pt(C₆F₅)₂(μ -SPPPh₂C₅H₅)₂].

2.4.3. 1:2 molar ratio

cis-[Pt(C₆F₅)₂(thf)₂] (0.02 g, 0.0297 mmol) and S=PPh₂C₅H₅ (0.0168 g, 0.0594 mmol) were mixed in CDCl₃ (0.6 ml) at -50°C . The initial ³¹P{¹H} NMR spectrum of this mixture at low temperature (-50°C) revealed the presence of **5** and **6** in a similar ratio together with the excess of S=PPh₂C₅H₅. When the temperature was increased to -10°C , the intensity of the signal due to **6** increased, giving a **5**/S=PPh₂(C₅H₅)/**6** ratio of \sim 1:3.5:2.8, and at $+20^{\circ}\text{C}$ only **6** (with traces of **4**) is observed. **6** could be isolated as a nearly pure solid and it was identified as [Pt(C₆F₅)₂(SPPPh₂C₅H₅)₂].

(**4**): (Signals taken of the 1:0.5 reaction mixture. Excess of *cis*-[Pt(C₆F₅)₂(thf)₂] was also observed). Anal. Calc. for C₅₈H₃₀F₂₀P₂Pt₂S₂ (1623.10): C, 42.92; H, 1.86; S, 3.95. Found: C, 42.79; H, 1.74; S, 3.70%. ¹H NMR (CDCl₃, 20°C): δ (ppm) 8.15, 7.8–7.2 (Ph), 6.89 (s, br) (CH=, C₅H₅), 3.94 (CH₂, C₅H₅). Two signals at 6.15 and 5.2 merely merging from the baseline could tentatively be assigned to CH= protons of Cp. A similar pattern was observed by lowering the temperature to -50°C . ³¹P{¹H} NMR (CDCl₃, 20°C): δ (ppm) 26.02 (s). ¹⁹F NMR (CDCl₃, 20°C): δ (ppm) -119.08 (m, ³J(Pt–F_o) \sim 388 Hz), -162.8 (t, F_p), -164.7 (m, F_m). IR (cm⁻¹) (Nujol): ν 802 (s), 800 (s) (X-sens C₆F₅), 575 (m) (P=S).

(**5**): (signals observed in the 1:1 reaction mixture at -10°C): ¹H NMR (CDCl₃): δ (ppm) 8.39 (overlapping of two doublets (Ph), the rest of the signals of the Ph

groups are overlapped with the signals due to compound **6**), 6.95(s), 6.44(s), 6.36 (s) (CH=, C₅H₅), 2.50 H_A, 2.24 H_B AB spin system, $J(\text{A–B}) = 24.59$ Hz (CH₂, C₅H₅). Assignment based on a ¹H–¹H COSY experiment at -10°C . ³¹P{¹H} NMR (CDCl₃): δ (ppm) 48.20 (s, ²J(Pt–P) = 159 Hz). ¹⁹F NMR (CDCl₃): δ (ppm) -118.1 (dm), -120.3 (m) F_o (³J(Pt–F_o) can not be unambiguously obtained), -160.6 (t, F_p), -160.9 (t, F_p), -163.4 (m, F_m).

(**6**): Anal. Calc. for C₄₆H₃₀F₁₀P₂PtS₂ (1093.90): C, 50.51; H, 2.76; S, 5.86. Found: C, 50.46; H, 2.58; S, 5.42%. ¹H NMR (CDCl₃, 20°C): δ (ppm) 7.73 (m, 8H), 7.47 (dd, 10H), 7.28 (m, 2H) (Ph), 6.98 (d, 2H), 6.87 (s, 2H), 6.57 (s, 2H) (CH=, C₅H₅), 3.36 (s, 4H, CH₂, C₅H₅). ³¹P{¹H} NMR (CDCl₃, 20°C): δ (ppm) 29.02 (s, $J(\text{Pt–P}) = 62.15$ Hz). ¹⁹F NMR (CDCl₃, 20°C): δ (ppm) -118.9 (dm, F_o, ³J(Pt–F_o) = 439 Hz), -165.2 (m, F_p + F_m). IR (cm⁻¹) (Nujol): ν 804 (vs), 792 (vs), (X-sens C₆F₅), 652 (vs), 605 (vs) (P=S).

2.5. Crystal data for complex

[Pt(C₆F₅)₂(μ -SPPPh₂C₅H₅)₂] 2CH₂Cl₂ (**4**)

Orange X-ray suitable crystals were obtained by slow diffusion of methanol into a dichloromethane solution at -20°C ($0.5 \times 0.2 \times 0.1$ mm³). Compound **4** crystallizes in the monoclinic space group *C2/c*, with $a = 24.4710(1)$, $b = 12.1984(2)$, $c = 20.9361(3)$ Å, $\beta = 110.923(1)$, $V = 5837.48(13)$ Å³, $Z = 4$, $D_{\text{calc}} = 2.040$ g cm⁻³, $\mu(\text{Mo–K}\alpha) = 5.203$ mm⁻¹. 12657 reflections (7560 independent reflections) ($1.78 < \theta < 30.23^{\circ}$, ω -scan, $T = 173(2)$ K) were measured on a Bruker Smart CCD using graphite monochromated Mo–K α radiation ($\lambda = 0.71073$ Å), overall completeness 86.9%. Data were corrected for absorption using empirical methods (SADABS) [14], maximum and minimum transmission 0.381638 and 0.213924, respectively. The structure was solved by direct methods (SHELXS-97) [15] and refined by full-matrix least square methods (SHELXL-97/2) [15] to final *R* factors of $R_1 = 0.0494$, $wR_2 = 0.1142$, Goodness-of-fit (*S*) = 0.993 for 4909 merged reflections with $I > 2\sigma(I)$. Hydrogen atoms were introduced on calculated positions and refined riding on their carrier atoms. All non-H atoms were refined with anisotropic thermal parameters. A final Fourier map showed no residual density outside -1.599 and 1.811 e Å⁻³ for **4**.

3. Results and discussion

The chemistry of thiolate titanocene derivatives has been the subject of our attention in recent years [16]. In this area we have recently prepared [13] new functionalised titanocene complexes [(η^5 -C₅H₄R)(η^5 -C₅H₄R')Ti(SPh)₂] [R,R' = SiMe₃, Ph₂P=E (E = S, O)] which have been shown to be excellent precursors to

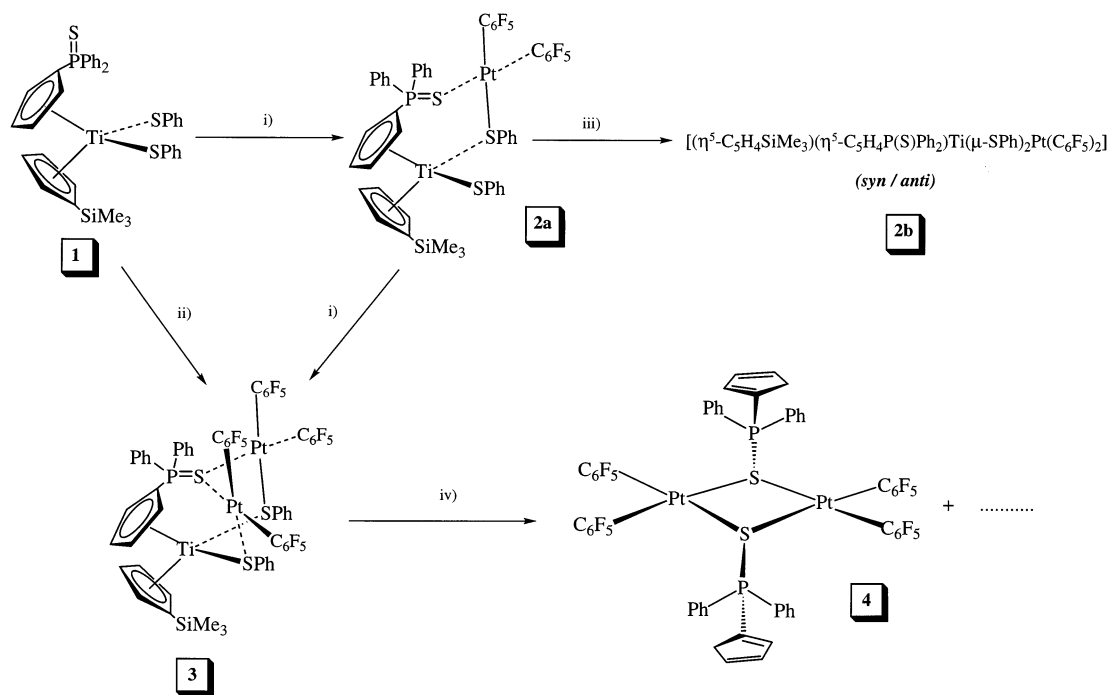
early–late bimetallic compounds. Thus, we have reported among others the synthesis and structural characterisation of a bimetallic TiPt green complex $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)(\text{SPh})\text{Ti}(\mu\text{-}1\eta^5\text{-C}_5\text{H}_4\text{P}(\text{S})\text{Ph}_2\text{-}2\kappa\text{S})\text{-}(\mu\text{-SPh})\text{Pt}(\text{C}_6\text{F}_5)_2]$ **2a** displaying a mixed thiolate-thiophosphorylcyclopentadienyl bridging system [17]. This complex, stable in solid state and in toluene solution, rearranges in CH_2Cl_2 solution to form the double thiolate bridged red isomer derivative **2b** (Scheme 1). In complex **2a**, which contains a terminal SPh fragment and a bridging $\eta^5\text{-}\kappa\text{S-C}_5\text{H}_4\text{P}(\text{S})\text{Ph}_2$ group, the sulphur atoms of both ligands still have free electron pairs and can behave as donor atoms. Therefore, and aiming to obtain higher nuclear derivatives, the reaction of $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)(\eta^5\text{-C}_5\text{H}_4\text{P}(\text{S})\text{Ph}_2)\text{Ti}(\text{SPh})_2]$ **1** with 2 molar equivalents of *cis*- $[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{thf})_2]$ (thf = tetrahydrofuran) was studied (Scheme 1).

When $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)(\eta^5\text{-C}_5\text{H}_4\text{P}(\text{S})\text{Ph}_2)\text{Ti}(\text{SPh})_2]$ **1** is treated with 2 equivalents of *cis*- $[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{thf})_2]$, the new trinuclear complex $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Ti}(\mu_3\text{-}1\eta^5\text{-C}_5\text{H}_4\text{P}(\text{S})\text{Ph}_2\text{-}2,3\kappa\text{S})(\mu\text{-SPh})_2\{\text{Pt}(\text{C}_6\text{F}_5)_2\}_2]$ **3** is obtained as a red microcrystalline solid in good yield (83%). As expected by using the binuclear complex **2a** as starting material, a clean reaction yielding complex **3** takes place almost immediately. Complex **3** can also be obtained from the reaction between **2b** and 1 equivalent of *cis*- $[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{thf})_2]$ but longer reaction time was required in this case. Although no crystals of **3** suitable for an X-ray study could be obtained, its characterisation by usual analytical and spectroscopic methods is straightforward. Thus, complex **3** gave satisfactory ele-

mental analysis and its IR spectrum showed the $\nu(\text{P}=\text{S})$ absorption at 636 cm^{-1} . It appears downwards shifted with respect to that observed in the mononuclear Ti complex **1** (656 cm^{-1}) and only slightly shifted related to the showed for the binuclear derivative **2a** (638 cm^{-1}) supporting coordination through the sulphur atom. The FAB^+ mass spectrum of **3** shows the molecular peak less a C_6F_5 unit (m/z 1575) in a good agreement with the calculated parent ion $[\text{M}-\text{C}_6\text{F}_5]^+$.

The phosphorous resonance at 28.2 ppm resembles to that observed in the binuclear complex **2a** (δ 26.7) and is significantly upfield shifted with respect to the uncoordinated $\text{P}=\text{S}$ entity of **1** (δ 35.7). The observed $^2J(\text{Pt}-\text{P})$ of $\sim 60\text{ Hz}$ is slightly smaller than that reported earlier for **2a** (65.8 Hz). The r.t. ^{19}F NMR spectrum confirms the presence of four non equivalent C_6F_5 groups unsymmetrically disposed with respect to their Pt coordination planes. Thus, the presence of eight F_{ortho} and four F_{para} resonances (five multiplets are seen in the F_{meta} region) of identical intensity clearly evidences that complex **3** is rigid on the NMR time scale. The absence of a symmetry average plane passing through the Ti centre is probably caused by crowding which prevents the free rotation of the $\text{C}_5\text{H}_4\text{SiMe}_3$ ring. Accordingly, the proton NMR spectrum exhibited in addition to the SiMe_3 (δ -0.09) and aromatic signals, six resonances in the cyclopentadienyl region confirming magnetically non-equivalent halves on either rings.

As mentioned before, attempts to obtain suitable crystals for X-ray diffraction studies in order to confirm the formulation of **3** failed in several solvent mixtures



Scheme 1.

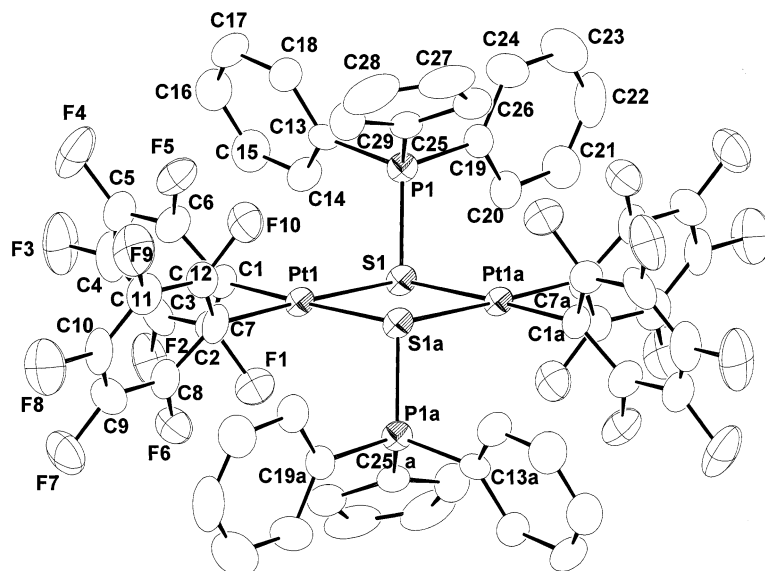


Fig. 1. ZORTEP [26] plot of $[\text{Pt}(\text{C}_6\text{F}_5)_2(\mu\text{-SPPPh}_2\text{C}_5\text{H}_5)]_2 \cdot 2\text{CH}_2\text{Cl}_2$ (**4**) with thermal ellipsoids at the 50% probability level.

and temperatures. On the other hand, by slow diffusion of MeOH in a solution of **3** in dichloromethane at low temperature (-20°C), pale orange crystals separated. An X-ray diffraction study reveals that under these conditions complex **3** decomposes yielding among others unidentified species, the binuclear diplatinum complex **4** which is formed by two identical $\text{Pt}(\text{C}_6\text{F}_5)_2$ fragments linked by two cyclopentadienyldiphenylphosphine sulphide ($\text{S}=\text{PPh}_2\text{C}_5\text{H}_5$) ligands (Fig. 1, Table 1). The sensibility of titanium compounds containing $\text{S}=\text{PPh}_2\text{C}_5\text{H}_4$ groups towards hydrolysis liberating $\text{S}=\text{PPh}_2\text{C}_5\text{H}_5$ ligand has been recently reported [18]. In this context, the formation of **4** is not unexpected and can be envisaged by hydrolysis of **3** and stabilisation of the resulting platinum fragments with $\text{S}=\text{PPh}_2\text{C}_5\text{H}_5$.

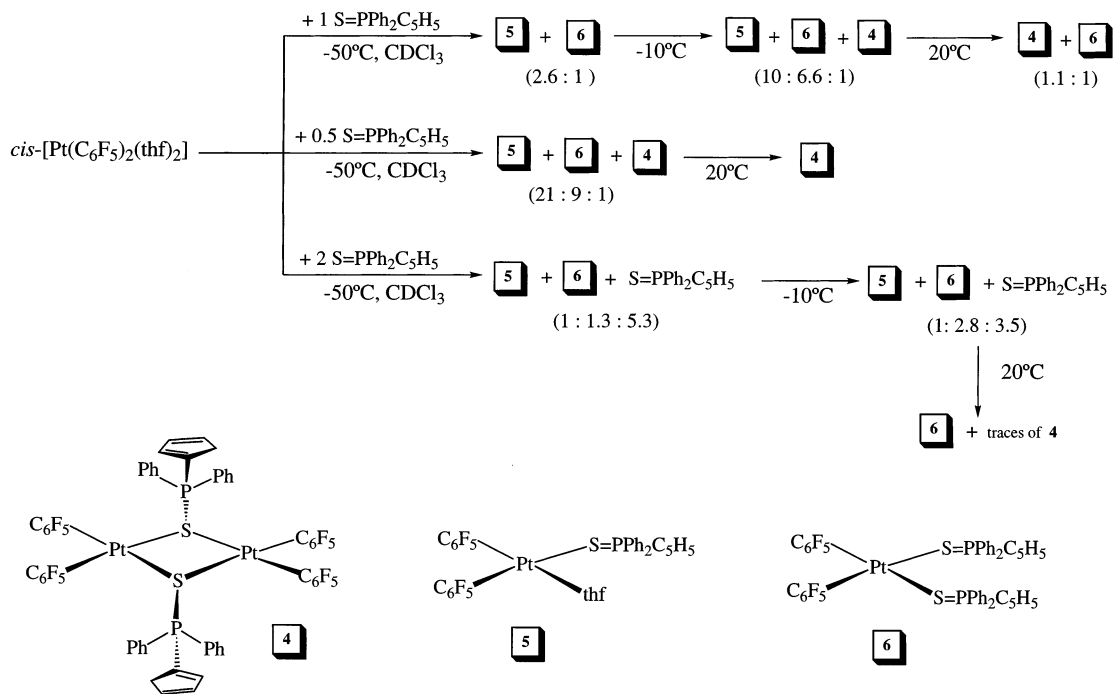
Although the synthesis of complexes containing tertiary phosphine sulphide bridging ligands has been previously reported [4i,5a,b] as far as we know, only two complexes have been structurally characterised: a trimer copper compound $[\text{Cu}(\text{SPMe}_3)\text{Cl}]_3$ [5c] and a tetrameric antimony derivative $[\text{SbBr}_3(\text{SPMe}_2\text{Ph})]_4$ [5d]. As can be observed in Fig. 1, which shows a view of the molecule, complex **4** is a dimer, and clearly, the most interesting feature of this complex is the presence of two $\text{S}=\text{PPh}_2\text{C}_5\text{H}_5$ molecules acting as bridging ligands through the sulphur atom. The molecule has a centre of inversion, and thus, the two platinum atoms are in identical environments. The coordination geometry of the platinum is nearly square planar, as expected [rms deviation of PtS_2C_2 plane, 0.0242 \AA , displacement of platinum $0.0090(31) \text{ \AA}$]. The Pt–C distances [$2.018(6)$, $2.042(7) \text{ \AA}$] are similar to those found in related complexes [16]. The central Pt_2S_2 core is roughly planar and exhibits angles at the Pt centres and at the sulphur atoms of $85.0(3)^\circ$ [$\text{C}(1)\text{Pt}(1)\text{C}(7)$] and $98.70(5)^\circ$

[$\text{Pt}(1)\text{S}(1)\text{Pt}(1\text{a})$], respectively. In the copper trimer $[\text{Cu}(\text{Me}_3\text{PS})\text{Cl}]_3$, in which the sulphur is involving in a six-member ring, the ring angles at S are bigger (105°) [5c]. However, in the tetramer $[\text{SbBr}_3(\text{SPMe}_2\text{Ph})]_4$, which also shows four membered rings, the angles observed at bridging sulphurs are $96.2(1)$ and $116.2(1)^\circ$ [5d]. The non-bonding platinum–platinum separation of $3.6660(5) \text{ \AA}$ can be compared to those observed for binuclear complexes having similar angles at the bridging atom such as $[\text{PtX}(\mu\text{-PPh}_2)(\text{PPh}_2\text{H})_2]$ [$\text{X} = \text{Cl}$ [19] $3.585(1) \text{ \AA}$, $\text{X} = \text{C}\equiv\text{CR}$ [20a] $3.649(1) \text{ \AA}$], $[\text{PEtPh}_3]_2\text{-}[\text{Pt}(\mu\text{-PPh}_2)(\text{C}_6\text{F}_5)_2]$ [$3.621(1) \text{ \AA}$] [20b] or $[\{\text{PtI}(\text{PPh}_3)(\mu\text{-SCH}_2\text{CH}_2\text{CMe}=\text{CH}_2)\}_2]$ [$3.539(1) \text{ \AA}$] [21] which also exhibit planar Pt_2X_2 ($\text{X} = \text{P}, \text{S}$) cores. The Pt–S bond lengths observed [$2.4094(17)$, $2.4227(17) \text{ \AA}$] are well in agreement with those reported for Pt_2S_2 cores in closely bridging thiolate complexes [21,22] but slightly longer than those observed in thiophosphoranyl platinum compounds, as for example in the cases $[\text{PtCl}(\text{PEt}_3)\text{-}\{\text{C}(\text{PPh}_2=\text{S})_3\text{-SS}'\}]$ [23] and $[\text{PtCl}(\text{PEt}_3)\{\text{Ph}_2\text{-PCH}_2\text{P}(\text{tBu})_2=\text{S}\}\text{-PS}]$ [3a] where the Pt–S lengths are

Table 1
Selected bond distances (\AA) and angles ($^\circ$) of $[\text{Pt}(\text{C}_6\text{F}_5)_2(\mu\text{-SPPPh}_2\text{C}_5\text{H}_5)]_2 \cdot 2\text{CH}_2\text{Cl}_2$ **4**^a

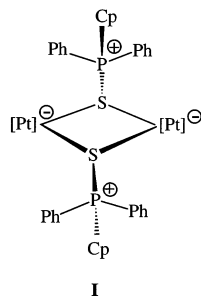
Pt(1)–C(1)	2.018(6)	Pt(1)–S(1a)	2.4227(17)
Pt(1)–C(7)	2.042(7)	P(1)–S(1)	2.072(3)
Pt(1)–S(1)	2.4094(17)	Pt⋯Pt	3.6660(5)
C(1)–Pt(1)–C(7)	85.0(3)	S(1)–Pt(1)–S(1a)	81.30(5)
C(1)–Pt(1)–S(1)	95.89(18)	Pt(1)–S(1)–Pt(1a)	98.70(5)
C(7)–Pt(1)–S(1a)	97.89(18)	P(1)–S(1)–Pt(1)	101.99(8)
P(1)–S(1)–Pt(1a)	100.92(9)		

^a Standard deviations in the last digits are in parentheses.



Scheme 2.

2.282(3) and 2.283(2) Å, respectively. The P(1)–S(1) distance of 2.072(3) Å is intermediate between the expected value for a P=S double bond (1.926–1.966 Å) and a P–S single bond (2.122 Å) [24] and, as expected, slightly longer than that observed for S-coordinated thiophosphoranyl groups [1,3,4,23]. The sum of the angles at sulphur is 301.6° showing that the sulphur is pyramidal. This fact points out some degree of bonding character as illustrated in



with a notable separation of charge, and it is in agreement with some recent theoretical *ab initio* studies that show the high tendency towards pyramidalization of S bridging atoms [25]. Concordant with this structural feature and with the presence of a centre of inversion, the two bridging cyclopentadienyldiphenylphosphine sulphide groups have an anti conformation with respect to each other, as expected, on steric grounds.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a sample of crystals of the same bath used for the crystallographic study of complex **4** exhibited a singlet at δ 26.00 and, probably due to poor resolution by low concentration, no plat-

inum satellites were observed. The corresponding proton spectrum also showed bad resolved resonances (δ 8.23–7.13 Ph; 6.93, 4.06 Cp) and some decomposition. With the aim of improving its characterisation in solution we attempted the synthesis of this diplatinum complex by reacting the solvated species $cis\text{-[Pt(C}_6\text{F}_5)_2(\text{thf})_2]$ directly with $\text{S=PPh}_2\text{C}_5\text{H}_5$. However, this alternative route was not as simple as we initially thought. Treatment of $cis\text{-[Pt(C}_6\text{F}_5)_2(\text{thf})_2]$ with 1 equivalent of $\text{S=PPh}_2\text{C}_5\text{H}_5$ in CH_2Cl_2 at r.t., gives a mixture of **4** and $cis\text{-[Pt(C}_6\text{F}_5)_2(\text{S=PPh}_2\text{C}_5\text{H}_5)_2]$ **6** (δ 29.02). We observed that if the reaction is carried out at lower temperature (0°C) or if there is defect of $\text{S=PPh}_2\text{C}_5\text{H}_5$, the formation of **4** is favoured (see Section 2). As expected, when $cis\text{-[Pt(C}_6\text{F}_5)_2(\text{thf})_2]$ reacts with two equivalents of $\text{S=PPh}_2\text{C}_5\text{H}_5$, the corresponding mononuclear complex $cis\text{-[Pt(C}_6\text{F}_5)_2(\text{S=PPh}_2\text{C}_5\text{H}_5)_2]$ **6** can be isolated as a white solid and characterised by usual methods. In particular, the presence of two $\nu(\text{P}=\text{S})$ and two X-sensitive C_6F_5 absorptions in its IR spectrum (C_{2v} symmetry $\text{A}_1 + \text{B}_1$ active modes) indicates the *cis*-geometry of the complex. This is also confirmed by ^{19}F NMR spectroscopy, which reveals that both C_6F_5 groups are equivalent.

These reactions are also monitored by NMR spectroscopy at low temperatures (see Scheme 2 and Section 2 for details). When the reaction in a molar ratio 1:1 was performed at -50°C , it could be observed that the formation of both complexes **4** and **6** takes place through the initial formation of a new species which, on the basis on NMR spectroscopy, was identified as the solvate complex $cis\text{-[Pt(C}_6\text{F}_5)_2(\text{S=PPh}_2\text{C}_5\text{H}_5)(\text{thf})]$ **5**.

This complex exhibited in the ^{31}P NMR spectrum a singlet resonance at δ 48.20 flanked by platinum satellites. The value of $^2J(^{195}\text{Pt}-^{31}\text{P})$ (159 Hz) observed is comparable to similar values previously reported for derivatives containing Pt–S=P units. Its ^{19}F NMR spectrum supports the presence of two types of C_6F_5 groups as is clearly evidenced by two triplets of identical intensity due to *para*-fluorine resonances. The corresponding ^1H NMR spectrum confirms the co-ordination of the $\text{S}=\text{PPh}_2\text{C}_5\text{H}_5$, which is particularly evident in the resonances due to the cyclopentadiene group. A ^1H – ^1H correlation spectrum of the 1:1 reaction mixture at a low temperature (-10°C) reveals, in addition to the olefinic resonances in the usual range, the presence of an AB system due to diastereotopic methylenic protons (δ H_A 2.50, H_B 2.24, $J(\text{A}-\text{B})=24.59$ Hz). A similar result was observed in the 1:2 molar ratio reaction but in this case, the formation of **4** seems to be less favoured and only traces of it were detected near to r.t. It should be noted that the precipitate was always observed in the NMR tubes; therefore, the ratio of the signals could be not the same as the proportion of the products. Finally, by monitoring the reaction with defect of $\text{S}=\text{PPh}_2\text{C}_5\text{H}_5$ (Pt:L molar ratio 1:0.5), only **4** and the excess of complex *cis*- $[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{thf})_2]$ remained when the temperature was raised to r.t.

In summary, in this study we have confirmed that the trinuclear titanium–diplatinum compound **3**, with a $\text{S}=\text{PPh}_2\text{C}_5\text{H}_4$ group η^5 -coordinated to the Ti centre, is easily hydrolysed giving rise to the $\text{S}=\text{PPh}_2\text{C}_5\text{H}_5$ ligand, which is stabilised with the platinum fragment forming the unusual double bis(cyclopentadienyldiphosphine sulphide) bridging diplatinum complex **4**. However, its direct synthesis starting from *cis*- $[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{thf})_2]$ and $\text{S}=\text{PPh}_2\text{C}_5\text{H}_5$ is not simple; the reaction leads to a mixture of **4** and the mononuclear product **6** and both complexes seem to be formed through the initial formation of the mononuclear solvate compound **5**.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure (of compound **4**) have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 139525. Copies of the data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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