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# Novel heterobimetallic titanium–platinum complexes. Crystal structure of $[(\eta^5\text{-}C_5H_4SiMe_3)(SPh)Ti(\mu,\eta^5\text{-}\kappa S\text{-}C_5H_4P(S)Ph_2)(\mu\text{-}SPh)Pt(C_6F_5)_2]$

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**Abstract**

The thiophosphorylcyclopentadienyl-thiolate complexes $[(\eta^5\text{-}C_5H_4R)(\eta^5\text{-}C_5H_4P(S)Ph_2)Ti(SPh)_2]$ react with *cis*-$[Pt(C_6F_5)_2(THF)_2]$ initially give the adducts $[(\eta^5\text{-}C_5H_4R)(SPh)Ti(\mu,\eta^5\text{-}\kappa S\text{-}C_5H_4P(S)Ph_2)(\mu\text{-}SPh)Pt(C_6F_5)_2]$ [R = $P(S)Ph_2$ (**1**); $SiMe_3$ (**4**)], which finally rearrange in solution to form the double thiolate-bridged derivatives $[(\eta^5\text{-}C_5H_4R)(\eta^5\text{-}C_5H_4P(S)Ph_2)Ti(\mu\text{-}SPh)_2Pt(C_6F_5)_2]$ [R = $P(S)Ph_2$ (**2**) (*syn*); $SiMe_3$ (**5**) (*syn*/*anti*)]. This paper presents the crystal structure of **4**, a complex displaying an unusual mixed thiolate-thiophosphorylcyclopentadienyl bridging system. In contrast, similar reactions of *cis*-$[Pt(C_6F_5)_2(THF)_2]$ with $[(\eta^5\text{-}C_5H_4R)(\eta^5\text{-}C_5H_4P(O)Ph_2)Ti(SPh)_2]$ (R = $P(O)Ph_2$; $SiMe_3$) only gives $[(\eta^5\text{-}C_5H_4R)(\eta^5\text{-}C_5H_4P(O)Ph_2)Ti(\mu\text{-}SPh)_2Pt(C_6F_5)_2]$ [R = $P(O)Ph_2$ (**3**) (*syn*); $SiMe_3$ (**6**) (*syn*/*anti* mixtures)] as expected due to the soft acid nature of the platinum centre. 

*Keywords:* Platinum; Titanium; Phosphorylcyclopentadienyl; Thiophosphorylcyclopentadienyl; Thiolate

## 1. Introduction

The coordination chemistry of phosphine chalcogenides has been known for a considerable time [1], but it still remains an area of research interest [2]. Of particular interest is the lability of the M–E (E = O, S) bonds in these complexes, as suggested by some authors [3], which seem to play an important role in catalytic processes where this type of compounds are involved. However, studies concerning the structure and reactivity of transition metal compounds bearing $[C_5H_4P(E)Ph_2^-]$ (E = O, S) ligands are extremely scarce. The only published work so far has been a few examples of heteronuclear complexes obtained by the use of phosphoryl and thiophosphoryl titanocene or ferrocene derivatives such as metalloligands, reported by us among other authors [4].

Although the chemistry of $(\eta^5\text{-}C_5H_4R)_2TiX_2$ (R = H, Me, $SiMe_3$; X = halogen or thiolate) has been widely developed [5], mixed titanocene derivatives containing donor and non-donor substituents in the rings of the molecule have been poorly explored [4a,6]. The substitution of the Cp ring protons in titanocene derivatives affects not only the solubility but also the steric and electronic properties of these systems [6c,7]. We have recently shown that the presence of $SiMe_3$ groups instead of $PPh_2$ ones in $(\eta^5\text{-}C_5H_4R)_2TiX_2$ (X = Cl, SR′) has a marked effect on the solubility and stability of these complexes [4a].

As an extension of our previous work on early–late heteronuclear systems [8], we report here the synthesis of novel heterobinuclear complexes with hetero $[(\eta^5\text{-}C_5H_4R)(SPh)Ti(\mu,\eta^5\text{-}\kappa S\text{-}C_5H_4P(S)Ph_2)(\mu\text{-}SPh)Pt(C_6F_5)_2]$ and homo $[(\eta^5\text{-}C_5H_4P(E)Ph_2)(\eta^5\text{-}C_5H_4R)Ti(\mu\text{-}SPh)_2Pt(C_6F_5)_2]$ [R = $SiMe_3$, $P(E)Ph_2$; E = O, S] bridging systems.

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## 2. Results and discussion

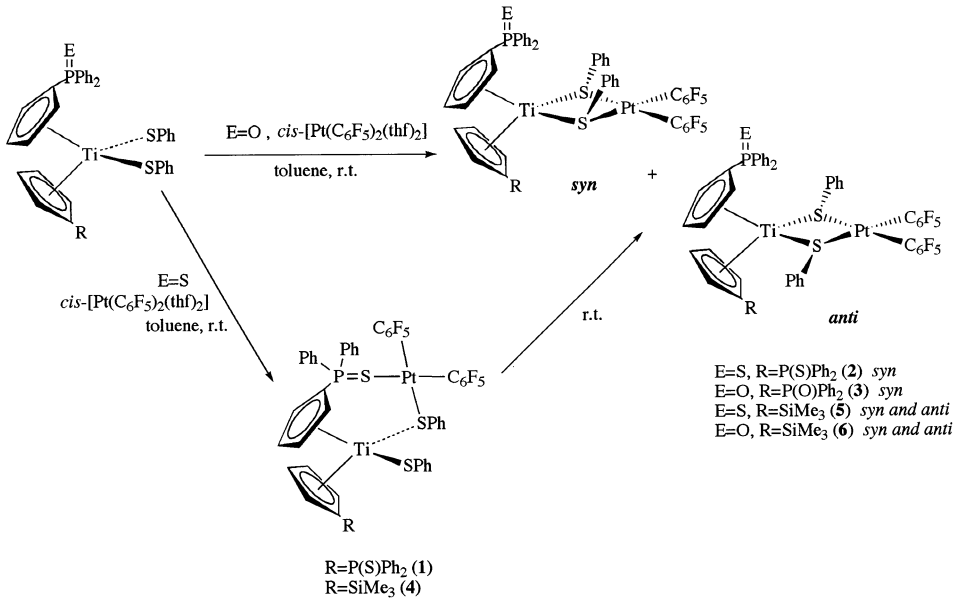
The treatment of metal compounds $[(\eta^5\text{-}C_5H_4P(S)Ph_2)(\eta^5\text{-}C_5H_4R)Ti(SPh)_2]$ containing four [R = $P(S)Ph_2$] or three (R = $SiMe_3$) potential sulphur donor atoms with an equimolecular amount of *cis*-$[Pt(C_6F_5)_2(THF)_2]$ in toluene at room temperature (r.t.) for a few minutes gives binuclear complexes stabilised by a mixed thiophosphorylcyclopentadienyl-thiolate bridging system $[(\eta^5\text{-}C_5H_4R)(SPh)Ti(\mu,\eta^5\text{-}\kappa S\text{-}C_5H_4P(S)Ph_2)(\mu\text{-}SPh)Pt(C_6F_5)_2]$ (R = $P(S)Ph_2$ (**1**); $SiMe_3$ (**4**)). It is noteworthy that while **4** was the only reaction product, compound **1** was invariably obtained with a small amount of complex $[(\eta^5\text{-}C_5H_4P(S)Ph_2)_2Ti(\mu\text{-}SPh)_2Pt(C_6F_5)_2]$ (**2**) (Scheme 1).

All attempts to purify compound **1** by crystallisation or a chromatographic column failed. Shortening of the reaction time to obtain a sole product did not give satisfactory results either; nevertheless, compound **2** was the only compound obtained from the mixture after stirring at r.t. during 15 h. This result evidences the spontaneous transformation of **1** into **2** (also observed in the solid state) by labilisation of the Pt–S bond involving the thiophosphorylcyclopentadienyl ligand. The nature of the solvent exerts an important role in the related transformation process of **4**. Thus, complex **4** did not change in a toluene solution after 20 h of stirring, while the use of dichloromethane gave complex $[(\eta^5\text{-}C_5H_4P(S)Ph_2)(\eta^5\text{-}C_5H_4SiMe_3)Ti(\mu\text{-}SPh)_2Pt(C_6F_5)_2]$ (**5**) as the only product after 10 min of stirring at r.t.

As was expected, the reaction between $[(\eta^5\text{-}C_5H_4P(O)Ph_2)(\eta^5\text{-}C_5H_4R)Ti(SPh)_2]$ [R = $P(O)Ph_2$, $SiMe_3$] and *cis*-$[Pt(C_6F_5)_2(THF)_2]$ carried out under the same conditions as the sulphur analogue gave complexes $[(\eta^5\text{-}C_5H_4P(O)Ph_2)(\eta^5\text{-}C_5H_4R)Ti(\mu\text{-}SPh)_2Pt(C_6F_5)_2]$ [R = $P(O)Ph_2$ (**3**), $SiMe_3$ (**6**)] directly. The lower tendency of $Pt^{II}$ (soft acid) to coordinate O-donor ligands (hard bases) must account for this behaviour. Compounds **2**, **3**, **5** and **6** are stable in the solid state but decompose progressively in solutions of most common solvents, even under nitrogen and at low temperature.

The formulation of **1** and **4** as Ti–Pt heterobinuclear compounds containing a thiolate group and a thiophosphorylcyclopentadienyl ligand bridging both metals was inferred from the spectroscopic data. Additionally, an X-ray diffraction study was carried out for complex $[(\eta^5\text{-}C_5H_4SiMe_3)(SPh)Ti(\mu,\eta^5\text{-}\kappa S\text{-}C_5H_4P(S)Ph_2)(\mu\text{-}SPh)Pt(C_6F_5)_2]$ (**4**), thus confirming the structure (Fig. 2).

Thus, the $^{31}$P-NMR spectrum of compound **1** showed two distinct singlet resonances due to the presence of inequivalent thiophosphoryl groups in the molecule. The lowfield signal ($\delta$ 33.29) remained almost unchanged when compared with the starting material ($\delta$ 35.5) and was assigned to the terminal thiophosphoryl group. The remaining singlet was significantly shifted to a lower frequency ($\delta$ 27.52) and was therefore attributed to the bridging $C_5H_4P(S)Ph_2$ group. Although no platinum satellites could be found for this latter signal, this assignment is in agreement with the chemical shift observed for the only phosphorous resonance in complex **4** ($\delta$ 26.68) which was also 9.02 ppm upfield shifted in relation with the precursor due to coordination with the platinum; it exhibited the expected two-bond coupling to platinum [$^2J$(Pt–P) = 65.8 Hz].




Scheme 1.

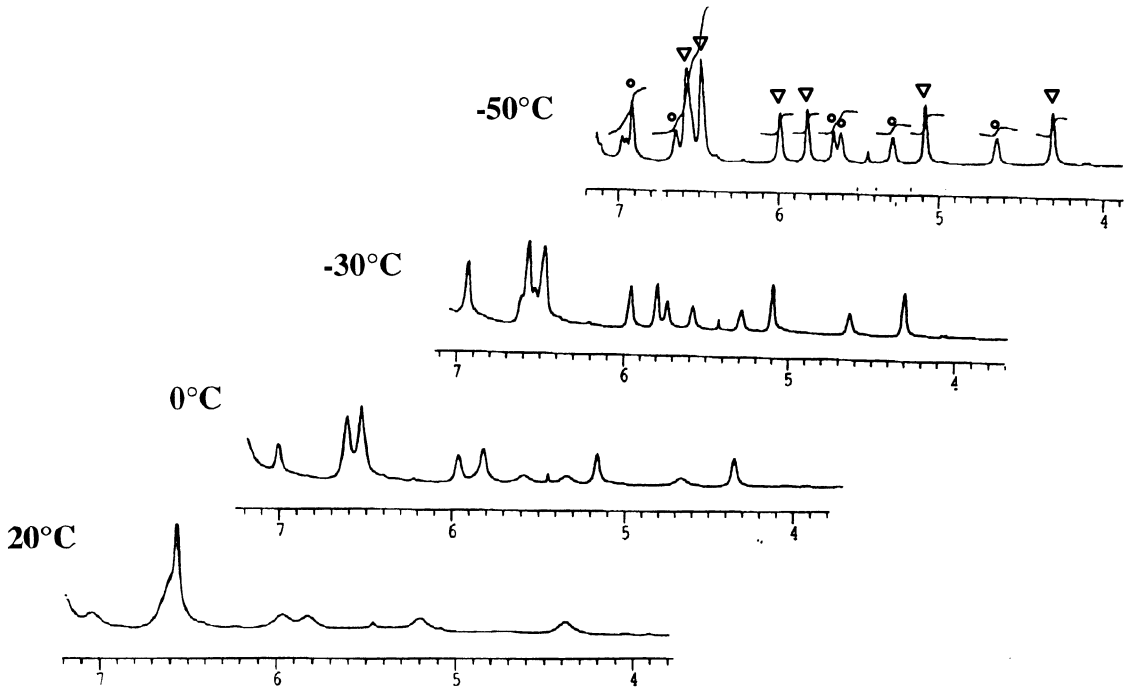



Fig. 1. NMR spectra of the complex $[(\eta^5\text{-}C_5H_4P(S)Ph_2)(\eta^5\text{-}C_5H_4SiMe_3)Ti(\mu\text{-}SPh)_2Pt(C_6F_5)_2]$ (**5**) (*syn* ○ and *anti* ▽) at different temperatures.

In the $^1$H-NMR spectra of both compounds, six (**1**) or seven (**4**) resonances were observed in the cyclopentadienyl region (1H was masked in the Ph region), indicating magnetically non-equivalent halves on both substituted cyclopentadienyl rings. The $^{19}$F-NMR spectra displayed signals confirming the presence of two inequivalent and rigid $C_6F_5$ groups due to the absence of a symmetry plane containing the Ti and Pt atoms in the molecule. Thus, although some of the expected resonances overlap in the $F_o$ and $F_m$ region (see Section 3 for details), the inequivalence of both rings can be easily inferred from the presence of two different triplets due to *para*-fluorine signals. Two peaks corresponding to coordinated and free P=S groups were exhibited in the IR spectrum of **1**.

The binuclear complexes with double thiolate bridge $[(\eta^5\text{-}C_5H_4P(E)Ph_2)(\eta^5\text{-}C_5H_4R)Ti(\mu\text{-}SPh)_2Pt(C_6F_5)_2]$ [$R = P(S)Ph_2$, E = S (**2**); $R = P(O)Ph_2$, E = O (**3**); $R = SiMe_3$, E = S (**5**); $R = SiMe_3$, E = O (**6**)] in solution may give a mixture of two isomers (*syn*/*anti*), such as has been observed in analogous compounds [9]. However, only the NMR spectra of the compounds containing two different substituted cyclopentadienyl ligands **5**–**6** showed the presence of both isomers in solution. For complexes **2** and **3** the presence of the *syn*(*endo*) isomer in solution is tentatively suggested on the basis of their $^{31}$P-NMR spectra. In keeping with this conformation, they exhibited two singlet resonances of equal intensity which appeared at similar $\delta$ values to the starting material, in agreement with the non-coordination of the thiophosphoryl ligands. It should be noted that if the rotation of the substituted $\eta^5\text{-}C_5H_4(E)PPh_2$ rings is prevented, then this pattern could also be compatible with the presence of the *anti* isomer. In fact, the $^{19}$F-NMR spectra shows two different sets of $C_6F_5$ signals, particularly evident in the *ortho* (four $F_o$) and *para* (two $F_p$) fluorine regions, indicating the inequivalence of both pentafluorophenyl groups; this seems to suggest that the rotation of the bulky substituted $\eta^5\text{-}C_5H_4(E)PPh_2$ rings is hindered.

One stretching band observed in the IR spectra [653 (P=S) **2**, 1180 (P=O) cm$^{-1}$ **3**], slightly shifted in relation to the starting material one, indicates non-coordination through the phosphoryl or thiophosphoryl groups. Additionally, two absorptions appearing at 790, 799, **2**, **3** are assigned to the X-sensitive vibration mode of the two mutually *cis* $C_6F_5$ groups [10].

As was mentioned above, the NMR data obtained at r.t. for complexes **5**–**6** was consistent with the presence of *syn*/*anti* isomers in solution. Studies carried out on binuclear Ti–M (M = Pt, Pd) compounds of the type $[(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}SR)_2ML_n]$ have always shown a higher preference for the *syn*(*endo*) isomer, not only in solution but also in the solid state [8b]. However, the NMR data obtained for **5**–**6** at low temperature ($-50$°C) indicated a higher proportion of the *anti*(*endo*) isomer [*anti*/*syn* 2:1 **5**, 1.5:1 **6**]. Upon increasing the temperature, only the cyclopentadienyl proton resonances of both isomers broadened, and at r.t. coalescence of the signals was only reached for complex **6**. For compound **5** (Fig. 1) four very broad signals corresponding to the major *anti* isomer were observed at r.t., suggesting that

the rate of *syn–anti* interconversion was still slow on the NMR time scale; due to the low stability of **5** in solution at higher temperature, no further experiments were carried out. In accordance with the formulation proposed, the $^{31}$P-NMR spectra exhibit two singlet resonances with similar $\delta$ values to the starting material, attributable to the *anti* and *syn* isomers, respectively. It should be mentioned that although the ratio of the *syn*/*anti* isomers was established using the integration of the $SiMe_3$ signals in the proton spectra, the assignment of the major component to the *anti* isomer was inferred from the $^{19}$F-NMR spectra. Both compounds exhibited in the *para*-fluorine region the three expected triplets due to $F_p$ signals of the three different types of $C_6F_5$. The two of identical intensity were assigned to the two non-equivalent $C_6F_5$ groups on the *anti* isomer and the remaining signal was therefore attributed to the *syn* isomer.

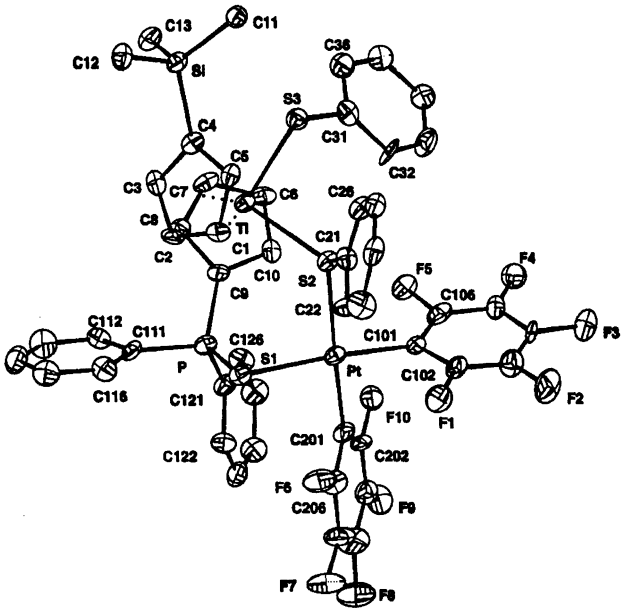



Fig. 2. A view of the molecular structure of [($\eta^5$-$C_5H_4SiMe_3$)(SPh)Ti($\mu$,$\eta^5$-$\kappa S$-$C_5H_4P(S)Ph_2$)($\mu$-SPh)Pt($C_6F_5$)$_2$] · $2H_2O$ (**4** · $2H_2O$).

Table 1
Selected bond lengths (Å) and angles (°) of complex **4**

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| Ti–S(2) | 2.527(4) | Ti–S(3) | 2.373(4) |
| Ti–Cp(1) | 2.0567 | Ti–Cp(2) | 2.0769 |
| Pt–S(1) | 2.401(3) | Pt–S(2) | 2.363(3) |
| Pt–C(101) | 2.003(12) | Pt–C(201) | 1.999(12) |
| S(1)–P | 1.966(5) | Pt···Ti | 4.245(10) |
| *Bond angles* | | | |
| S(2)–Ti–S(3) | 91.68(13) | Cp(1)–Ti(1)–Cp(2) | 131.66 |
| S(1)–Pt–S(2) | 93.63(11) | S(1)–Pt–C(101) | 174.7(4) |
| S(2)–Pt–C(201) | 173.7(4) | C(201)–Pt–C(101) | 88.9(5) |

### *2.1. Crystal structure of [($\eta^5$-$C_5H_4SiMe_3$)(SPh)Ti-($\mu$,$\eta^5$-$\kappa S$-$C_5H_4P(S)Ph_2$)($\mu$-SPh)Pt($C_6F_5$)$_2$] · $2H_2O$ (4 · $2H_2O$)*

The molecular structure of **4** is illustrated in Fig. 2 and selected bond lengths and angles are given in Table 1. The complex crystallises together with two molecules of water.

The titanium atom shows a pseudotetrahedral geometry formed by the two centroids of the substituted cyclopentadienyl ligands and two sulphur atoms of the thiolate ligands. One of these sulphur atoms and the sulphur of the $Ph_2P$=S ring substituent, together with the $C_{ipso}$ atoms of each $C_6F_5$ group, comprise a distorted square planar environment around the platinum atom. In this complex, the terminal (2.373(4) Å) and bridging (2.527(4) Å) Ti–S lengths, are comparable to those previously observed for related distances in the heterobridged compound [($\eta^5$-$C_5H_4SiMe_3$)(SC≡CBu$^t$)-Ti($\mu$,$\eta^5$-$\kappa P$-$C_5H_4PPh_2$)($\mu$-SC≡CBu$^t$)Pt($C_6F_5$)$_2$] [2.366(4), 2.532(4) Å] [8c] and similar to those reported for other terminal [11,12] or thiolate-bridged [8b] titanium complexes.

A longer distance was observed for the Pt–S(1) bond [2.401(3) Å] when compared with the Pt–S(2) one [2.363(3) Å], as well as the slight lengthening of the P=S distance by coordination to the Pt centre [1.966(5) Å] in comparison to those shown by the complexes [($\eta^5$-$C_5H_4P(S)Ph_2$)$_2$Ti(SPh)$_2$] [1.944 and 1.942 Å] [6a], [($\eta^5$-$C_5H_4P(S)Ph_2$)($\eta^5$-$C_5H_4SiMe_3$)TiCl$_2$] [1.944 Å] [6a]. This suggests that the interaction between the platinum and the $P(S)Ph_2$ group is rather weak and may explain the labilisation of the bond in solution. A study on this type of process has been carried out for complex [PtCl(PEt$_3$){P(S)Ph$_2$}$_2$CH] [13], whose crystalline structure showed a Pt–S distance of 2.39 Å.

The S(2)–Ti–S(3) and Cp–Ti–Cp angles [91.68(13) and 131.66°] are comparable to those found in [($\eta^5$-$C_5H_4SiMe_3$)(SC≡CBu$^t$)Ti($\mu$,$\eta^5$ - $\kappa P$ - $C_5H_4PPh_2$)($\mu$-SC≡CBu$^t$)Pt($C_6F_5$)$_2$] [89.39(12) and 133.5°] [8c], although bigger S–Ti–S angles have been reported for related mononuclear or bridged bis(thiolate) complexes [($\eta^5$-$C_5H_4P(S)Ph_2$)$_2$Ti(SPh)$_2$] [99.26°] [6a], [(CO)$_4$Mo($\mu$,$\eta^5$-$\kappa P$-$C_5H_4PPh_2$)Ti($\mu$-SPh)$_2$Pt($C_6F_5$)$_2$] [97.14°] [8d], [($\eta^5$-$C_5H_4SiMe_3$)$_2$Ti(SC$_6F_5$)$_2$] [100.6(1)°] [14] and [($\eta^5$-$C_5H_4SiMe_3$)$_2$Ti($\mu$-SPh)$_2$Pd($C_6F_5$)$_2$] [95.7(2)°] [8b]. A very long Ti···Pt distance [4.245(10) Å] was found, indicating no interaction between the two metals.

## 3. Experimental

All manipulations were carried out using standard Schlenk techniques under an atmosphere of oxygen-free argon [15]. Solvents were purified according to standard

procedures [16]. The starting materials ($\eta^5$-$C_5H_4R$)($\eta^5$-$C_5H_4R'$)Ti(SPh)$_2$ (R = R′ = P(S)Ph$_2$; R = R′ = P(O)Ph$_2$; R = P(S)Ph$_2$, R′ = SiMe$_3$, R = P(O)Ph$_2$, R′ = SiMe$_3$) [6a] and *cis*-[Pt($C_6F_5$)$_2$(THF)$_2$] [17] were prepared by literature methods and all other reagents were commercially available.

IR spectra (range 4000–400 cm$^{-1}$) were recorded on a Perkin–Elmer 1600 FT spectrophotometer. Elemental analyses were performed with a Perkin–Elmer 2400 microanalyzer. NMR spectra on Bruker AMX-300 or ARX-300 with chemical shifts reported in ppm relative to external standards ($SiMe_4$ for $^1$H, $CFCl_3$ for $^{19}$F and $H_3PO_4$ for $^{31}$P).

### 3.1. Synthesis

#### 3.1.1. [($\eta^5$-$C_5H_4R$)(SPh)Ti($\mu$,$\eta^5$-$\kappa S$-$C_5H_4P(S)Ph_2$)-($\mu$-SPh)Pt($C_6F_5$)$_2$] [R = P(S)Ph$_2$ (**1**); SiMe$_3$ (**4**)]

To a solution of [($\eta^5$-$C_5H_4P(S)Ph_2$)$_2$Ti(SPh)$_2$] (0.09 g, 0.11 mmol) in toluene (20 cm$^3$) was added *cis*-[Pt($C_6F_5$)$_2$(THF)$_2$] (0.09 g, 0.14 mmol). After stirring the mixture for 5 min, the solvent was removed in vacuo to yield a green solid that was mainly complex **1** (95% by $^{31}$P-NMR spectroscopy).

Data for **1**: $\nu_{max}$ (cm$^{-1}$) (KBr) 654w, 636w (P=S), 802s, 792s ($C_6F_5$). $^1$H-NMR ($CDCl_3$) $\delta$ 8.88 (m), 7.91–7.08 (m) (30H $C_6H_5$ and 1H $C_5H_4$), 7.00, 6.90, 6.73, 6.46, 6.27, 4.55 (m, 7H, ratio 1:2:1:1:1:1, $C_5H_4$). $^{31}$P{$^1$H}-NMR ($CDCl_3$) $\delta$ 33.29 [s, P(S)Ph$_2$], 27.52 [s, P(S)Ph$_2$]. $^{19}$F-NMR [$CDCl_3$, $^3J$(Pt–$F_o$) (Hz) in parentheses] $\delta$ −118.3 (dm, 1F), −119.6 (overlapping of two doublets, 2F), −120.5 [dm, (450), 1F] ($F_o$), −163.7 (t, 1F, $F_p$), −163.9 (t, 1F, $F_p$), −165.1 (m, 3F, $F_m$), −166.3 (m, 1F, $F_m$). The impurification of **1** with traces of compound **2** precludes the achievement of a reliable elemental analysis.

Data for **4**: This complex was prepared in a similar way to **1**. In this case **4** was precipitated, as a green solid, by addition of *n*-hexane and cooling at −20°C (65%). (Found: C, 48.45; H, 3.11. $C_{49}H_{37}F_{10}PPtS_3SiTi$ requires C, 48.48; H, 3.07%). $\nu_{max}$ (cm$^{-1}$) (KBr) 638m (P=S), 802s, 791s ($C_6F_5$). $^1$H-NMR (20°C, $CDCl_3$) $\delta$ 8.71 (br), 7.95–7.14 (m) (20H $C_6H_5$ and 1H $C_5H_4$), 6.96, 6.66, 6.56, 6.38, 5.80, 5.60, 5.40 (s, 7H, $C_5H_4$), 0.10 (s, 9H, $SiMe_3$); similar spectra were obtained at −50°C. $^{31}$P{$^1$H}-NMR ($CDCl_3$) $\delta$ 26.68 [s, P(S)Ph$_2$, $^2J$(Pt–P) = 65.8 Hz]; (−50°C, $CDCl_3$) 26.71 [s, P(S)Ph$_2$]. $^{19}$F-NMR [$CDCl_3$, $^3J$(Pt–$F_o$) (Hz) in parentheses] $\delta$ −118.0 [dm, 1F, (440)], −119.5 [overlapping of two doublets, 2F, (461)], −120.3 [dm, 1F, (428)] ($F_o$), −163.9 (t, 1F, $F_p$), −164.3 (t, 1F, $F_p$), −165.2 (m, 1F, $F_m$), −165.4 (m, 2F) (partial overlapping of two $F_m$), −166.4 (m, 1F, $F_m$); (−50°C, $CDCl_3$) −118.4 [d, 1F, (443)], −120.0 [d, 1F, (480)], −120.4 [d, 1F, (460)], −120.75 [d, 1F, (405)] ($F_o$), −163.4 (t, 1F, $F_p$), −163.7 (t, 1F, $F_p$), −164.8 (m, 3F, $F_m$), −165.9 (m, 1F, $F_m$).

#### 3.1.2. [($\eta^5$-$C_5H_4P(E)Ph_2$)($\eta^5$-$C_5H_4R$)Ti($\mu$-SPh)$_2$Pt-($C_6F_5$)$_2$] [R = P(S)Ph$_2$, E = S (**2**); R = SiMe$_3$, E = S (**5**)]

A toluene solution (15 cm$^3$) of [($\eta^5$-$C_5H_4P(S)Ph_2$)-(SPh)Ti($\mu$,$\eta^5$ - $\kappa S$ - $C_5H_4P(S)Ph_2$)($\mu$-SPh)Pt($C_6F_5$)$_2$] (**1**) (0.15 g, 0.11 mmol) was stirred for 15 h at r.t. The resulting red solution was filtered through Celite, the solvent removed to dryness and the residue obtained crystallised in 1:1 diethyl ether–pentane at −20°C to yield red crystals of **2** (0.12 g, 83%).

Data for **2**: (Found: C, 51.30; H, 3.33. $C_{58}H_{38}F_{10}P_2PtS_4Ti$ requires C, 51.30; H, 2.82%). $\nu_{max}$ (cm$^{-1}$) (KBr) 653w (P=S), 799m, 790m ($C_6F_5$). $^1$H-NMR ($CDCl_3$) $\delta$ 7.92–7.15 (m, 30H, $C_6H_5$), 7.07, 6.56, 6.38, 6.01, 5.76, 5.55, 4.51 (m, 8H, ratio 1:2:1:1:1:1:1, $C_5H_4$). $^{31}$P{$^1$H}-NMR ($CDCl_3$) $\delta$ 35.32 [s, P(S)Ph$_2$], 34.61 [s, P(S)Ph$_2$]. $^{19}$F-NMR [$CDCl_3$, $^3J$(Pt–$F_o$) (Hz) in parentheses] $\delta$ −116.6 (dm), −117.3 (m), −118.1 (dm), −118.4 (dm) ($F_o$), −161.7 (t, 1F, $F_p$), −161.9 (t, 1F, $F_p$), −163.2 (m, 2F), −164.2 (m, 1F), −164.5 (m, 1F) ($F_m$).

Data for **5**: Complex **5** was prepared following the procedure described for the synthesis of **2** but using dichloromethane as solvent and 10 min of stirring (90%). (Found: C, 48.37; H, 3.08. $C_{49}H_{37}F_{10}PPtS_3SiTi$ requires C, 48.48; H, 3.07%). $\nu_{max}$ (cm$^{-1}$) (KBr) 656m (P=S), 798s, 788s ($C_6F_5$). $^1$H-NMR (−50°C, $CDCl_3$) $\delta$ 7.9 (m), 7.6–7.12 (m) (20H $C_6H_5$ and 1H $C_5H_4$ *syn* isomer), 6.90, 6.63, 5.64, 5.60, 5.26, 4.62 (br, 7H, ratio 2:1:1:1:1:1, $C_5H_4$ *syn* isomer), 6.56, 6.47, 5.97, 5.80, 5.06, 4.28 (br, 8H, ratio 2:2:1:1:1:1, $C_5H_4$ *anti* isomer), 0.29 (s, 9H, $SiMe_3$ *syn* isomer), 0.18 (s, 9H, $SiMe_3$, *anti* isomer) (ratio *syn*:*anti* 1:2); (20°C, $CDCl_3$) $\delta$ 7.9 (br), 7.49 (br), 7.28 (br) ($C_6H_5$), 6.56, 5.96, 5.83, 5.19, 4.38 (br, $C_5H_4$, *syn* and *anti* isomers), 0.30 (br, $SiMe_3$, *syn* isomer), 0.21 (br, $SiMe_3$, *anti* isomer) (ratio *syn*:*anti* 1:1.7). $^{31}$P{$^1$H}-NMR (−50°C, $CDCl_3$) $\delta$ 35.51 [s, P(S)Ph$_2$, *anti* isomer], 35.45 [s, P(S)Ph$_2$, *syn* isomer] (ratio *syn*:*anti* 1:2); (20°C, $CDCl_3$) 35.38 [s, P(S)Ph$_2$, *anti* isomer], 35.16 [s, P(S)Ph$_2$, *syn* isomer] (ratio *syn*:*anti* 1:2). $^{19}$F-NMR [$CDCl_3$, $^3J$(Pt–$F_o$) (Hz) in parentheses] at −50°C, $\delta$ −117.4 [dm, (413)], −117.95 [dm, (424)], −118.15 (dm), −118.3 (dm, (418)] ($F_o$, *syn* and *anti* isomers), −161.44, −161.48 (overlapping of two triplets, $F_p$, *anti* isomer), −161.66 (t, $F_p$, *syn* isomer), −162.6 (m), −163.9 (m) ($F_m$, ratio 1:1) (ratio *syn*:*anti* could not be established); at 20°C, $\delta$ −117.45 to −117.7 (br), −118.2 (d), −118.5 (br) (complex region, $F_o$), −162.02 (t), −162.09 (t) (overlapping of $F_p$), −163.5 (br), −164.6 (m) ($F_m$, ratio 1:1, *syn* and *anti* isomers).

*3.1.3. [($\eta^5$-$C_5H_4P(E)Ph_2$)($\eta^5$-$C_5H_4R$)Ti($\mu$-$SPh)_2$Pt-$(C_6F_5)_2$] [R = $P(O)Ph_2$, E = O (**3**); R = $SiMe_3$, E = O (**6**)]*

In a similar reaction to that of compound **1**, [($\eta^5$-$C_5H_4P(O)Ph_2)_2Ti(SPh)_2$] (0.15 g, 0.18 mmol) was treated with one equivalent of *cis*-[$Pt(C_6F_5)_2(THF)_2$] (0.12 g, 0.18 mmol). After 10 min stirring, the solution was filtered through Celite and concentrated (ca. 10 $cm^3$). By addition of *n*-hexane (5 $cm^3$) a red crystalline solid corresponding to **3** was isolated after filtration and dryness in vacuo (70%).

Data for **3**: (Found: C, 52.48; H, 2.85. $C_{58}H_{38}F_{10}O_2P_2PtS_2Ti$ requires C, 52.54; H, 2.89%.) $\nu_{max}$ ($cm^{-1}$) (KBr) 1180m (P=O), 799s, 790s ($C_6F_5$). $^1$H-NMR ($CDCl_3$) $\delta$ 7.93–7.11 (m, 30H $C_6H_5$ and 2H $C_5H_4$), 6.58, 6.48, 6.43, 6.21, 4.98, 4.42 (m, 6H, $C_5H_4$). $^{31}P\{^1H\}$-NMR ($CDCl_3$) $\delta$ 22.12 [s, $P(O)Ph_2$], 20.42 [s, $P(O)Ph_2$]. $^{19}$F-NMR ($CDCl_3$, $^3J$(Pt–$F_o$) (Hz) in parentheses] $\delta$ −117.6 (dm), −117.9 (m), −118.1 (dm), −118.3 (m) ($F_o$), −161.8 (t, overlapping of two triplets, 2F, $F_p$), −163.3 (m, 2F), −164.8 (m, 2F) ($F_m$).

Data for **6**: Following the same procedure described above for the preparation of **3**, pure samples of complex **6** were obtained after recrystallisation from 1:1 diethyl ether–pentane (73%). (Found: C, 49.15; H, 3.16. $C_{49}H_{37}F_{10}PPtS_2OSiTi$ requires C, 49.13; H, 3.11%.) $\nu_{max}$ ($cm^{-1}$) (KBr) 1180m (P=O), 798s, 788s ($C_6F_5$). $^1$H-NMR (−50°C, $CDCl_3$) $\delta$ 7.89, 7.77, 7.60, 7.46, 7.29, 7.16 (m, $C_6H_5$), 6.91 (t), 6.88 (m), 6.71 (m), 6.54 (br), 6.33 (br), 6.05 (br), 5.96 (m), 5.61 (m), 5.02 (br), 4.88 (br), 4.53 (br), 4.27 (br) ($C_5H_4$ *syn* and *anti* isomers), 0.39 (s, $SiMe_3$, *anti* isomer), 0.12 (s, $SiMe_3$, *syn* isomer) (ratio *syn*:*anti* 1:1.5); (20°C, $CDCl_3$) 7.53–7.25 (m, $C_6H_5$), 6.54 (br, $C_5H_4$, *syn* and *anti* isomers), 0.40 (s, $SiMe_3$, *anti* isomer), 0.22 (s, $SiMe_3$, *syn* isomer) (ratio *syn*:*anti* 1:1.3). $^{31}P\{^1H\}$-NMR (−50°C, $CDCl_3$) $\delta$ 24.49 [s, $P(O)Ph_2$, *anti* isomer], 22.69 [s, $P(O)Ph_2$, *syn* isomer] (ratio *syn*:*anti* 1:1.5); (20°C, $CDCl_3$) 22.67 [s, $P(O)Ph_2$, *anti* isomer], 21.1 [s, $P(O)Ph_2$, *syn* isomer] (ratio *syn*:*anti* 1:1.3). $^{19}$F-NMR (−50°C, $CDCl_3$, $^3J$(Pt–$F_o$) (Hz) in parentheses] $\delta$ −117.8 (dm), −118.1 (dm), −118.3 (dm), −118.6 (dm) (complex region $F_o$, *syn* and *anti* isomers), −161.41, −161.49 ($F_p$, *anti* isomer), −161.4 ($F_p$, *syn* isomer) (overlapping of three triplets), −162.7 (m), −164.1 (m) ($F_m$, ratio 1:1, *syn* and *anti* isomers) (ratio *syn*:*anti* could not be established); (20°C, $CDCl_3$) −117.7 (m), −118.2 (dm), −118.5 (dm) ($F_o$), −162.1 (m, $F_p$), −162.6 (br), −164.5 (m) ($F_m$, *syn* and *anti* isomers).

*3.2. X-ray structural determination for **4**·$2H_2O$*

Data for $C_{49}H_{37}F_{10}PPtS_3SiTi \cdot 2H_2O$ (a dark red crystal) were collected at 160 K on a Stoe Imaging Plate Diffraction System equipped with an Oxford Cryosystems Cryostream cooler device and using a graphite-monochromated Mo–$K_\alpha$ radiation ($\lambda = 0.71073$ Å). The crystal to detector distance was 100 mm, owing to low diffraction intensity at $\theta > 22°$. A final unit cell parameters were obtained by least-squares refinement of a set of 5000 reflections and a crystal decay was monitored by measuring 200 reflections per image. Any fluctuations of the intensity were observed over the course of the data collection. Numerical absorption correction [18] was applied on the data by using a set of symmetry equivalent reflections selected with the criterion [$I > 3\sigma(I)$] such that all directions are equally represented, the min and max transmissions are, respectively, 0.242 and 0.702. 26 606 reflections were collected [5587 unique reflections with $I > 2\sigma(I)$, $R_{int} = 0.0899$]. Crystal data are as follows: crystal size $0.30 \times 0.20 \times 0.05$ $mm^3$, monoclinic, space group $P2_1/c$, $a = 23.207(4)$, $b = 11.2671(18)$, $c = 21.249$ (3) Å, $\beta = 110.690(17)°$, $V = 5197.9(14)$ $Å^3$, $Z = 4$, $D_{calc} = 1.592$ $g \cdot cm^{-3}$, $\mu$(Mo–$K_\alpha$) = 3.089 $mm^{-1}$, $F(000) = 2456$. The structure was solved by direct methods using SIR92 [19], and refined by least-squares on a $F^2$ with the aid of SHELXL97 [20], by minimising the function $\Sigma[w(F_o^2 - F_c^2)^2]$. The atomic scattering factors were taken from the International Tables for X-ray Crystallography [21]. The final $R(F)$ value was 0.0563 [$wR(F^2) = 0.1365$]. All hydrogen atoms were located on a difference Fourier map, and refined with a riding model. Non-hydrogen atoms were anisotropically refined and in the last cycles of refinement a weighting scheme was used [$w = 1/[\sigma^2(F_o^2) + (0.0708P)^2 + 59.1701P]$, where $P = (F_o^2 + 2F_c^2)/3$. Drawing of the molecules was performed with the program CAMERON [22] (ellipsoids at the 50% probability level).

## 4. Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 121763. Copies of this information 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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