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Synthesis and characterization of oxo- and thiophosphorylcyclopentadienyl Ti(IV) thiolate complexes. Crystal structures of $[(\eta^5\text{-}C_5H_4P(S)Ph_2)(\eta^5\text{-}C_5H_4SiMe_3)TiCl_2]$ and $[(\eta^5\text{-}C_5H_4P(S)Ph_2)_2Ti(SPh)_2]\cdot C_4H_{10}O$

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Abstract

New titanium (IV) complexes containing diphenyloxo- or diphenylthiophosphorylcyclopentadienyl ligands are obtained by reaction of diphenylphosphinocyclopentadienyl derivatives with the appropriate oxidizer (S_8 or H_2O_2). The crystal structures of $[(\eta^5\text{-}C_5H_4P(S)Ph_2)(\eta^5\text{-}C_5H_4SiMe_3)TiCl_2]$ **3** and $[(\eta^5\text{-}C_5H_4P(S)Ph_2)_2Ti(SPh)_2]\cdot C_4H_{10}O$ **7** indicate in both cases, a pseudo-tetrahedral arrangement around the titanium atom. The two SPh ligands in compound **7** are orientated in opposite sites of the TiS_2 plane, which suggests an *anti* conformation for this molecule.

Keywords: Titanium; Thiolate; Cyclopentadienyl

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1. Introduction

Organotransition metal compounds with ligands containing sulfur atoms have been a subject of considerable interest in recent years on view of their importance to biological systems [1] and catalytic processes [2]. The chemistry of cyclopentadienyl (Cp) Ti(IV) thiolate derivatives is being also explored due to the ability of these species to act as metalloligands towards different metal fragments [3]. In addition, structural studies carried out on bent metallocene thiolates have pointed out the conformational preferences exhibited by these complexes depending on the S–M–S angle [4].

The presence of substituted Cp ligands is known to induce changes in the reactivity and stability of these complexes when compared with those bearing unsubstituted rings [5]. But although many compounds of formula $[(\eta^5\text{-}C_5H_4R)(\eta^5\text{-}C_5H_5)TiX_2]$ (R = Me, ^{t}Bu, $SiMe_3$, $CH{=}CH_2$, etc.) have been reported [6], data on analogous species with mixed monosubstituted Cp ligands are scarce. Derivatives of these type containing a donor-substituent group might undoubtedly prove an useful way to bond to other metal fragments. In this context recently Jutzi et al. [7] have synthesized the new complex $[(\eta^5\text{-}C_5H_4CH_2CH_2N^iPr_2)(\eta^5\text{-}C_5H_4SiMe_3)TiCl_2]$.

By the other hand, the coordination chemistry of the phosphine oxides and sulphides has been a subject of numerous studies over the years [8], however little work has been done on related oxo- and thiophosphorylcyclopentadienyl ligands with the exception of ferrocene systems containing these ligands [9].

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In connection with our current studies on thiolate titanium (IV) derivatives, we report the syntheses and characterization of compounds [(η^5-$C_5H_4PPh_2$)(η^5-$C_5H_4SiMe_3$)TiX_2] (X = Cl **1**; X = SPh **2**) and the new diphenyloxo- and diphenylthiophosphorylcyclopentadienyl complexes of formula [(η^5-$C_5H_4P(E)Ph_2$)(η^5-$C_5H_4SiMe_3$)TiX_2] (E = S, X = Cl **3**; E = O, X = SPh **4**; E = S, X = SPh **5**) and [(η^5-$C_5H_4P(E)Ph_2$)$_2TiX_2$] (E = S, X = Cl **6**; E = S, X = SPh **7**; E = O, X = SPh **8**).

For compounds [(η^5-$C_5H_4P(S)Ph_2$)(η^5-$C_5H_4SiMe_3$)$TiCl_2$] **3** and [(η^5-$C_5H_4P(S)Ph_2$)$_2Ti(SPh)_2$]·$C_4H_{10}O$ **7** X-ray diffraction studies have been carried out.

2. Results and discussion

The ability of the thiolate titanocene species to act as metalloligands in the synthesis of heteronuclear compounds has been studied by Stephan et al. among others [3]. It is clear that the presence of a donor group as substituent in the Cp rings of these titanocene derivatives could also facilitate coordination to other metal fragments through these ligands. Nevertheless since Poilblanc et al. [10] reported the synthesis of compounds (η^5-$C_5H_4(CH_2)_nPPh_2$)$_2MCl_2$ (M = Ti, Zr) no much chemistry has been developed in this direction. Very recently we have studied ([3]b, [11]) the coordinative competition between P and S atoms towards Mo, Pt and Pd fragments in complexes bis[(diphenylphosphino)cyclopentadienyl] bis(chloride) or bis(thiolate) Ti(IV). Our experience with these derivatives reveals their unstability in solution. In contrast the presence in the Cp rings of no donor groups, such as $SiMe_3$, seems to improve the stability and to enhance the solubility of the complexes [12].

In addition, data on mixed substituted Cp derivatives of Ti(IV) being one of them a donor-substituent group are scarce. Jutzi et al. [7] have just recently reported the synthesis and characterization of the compound [(η^5-$C_5H_4CH_2CH_2N^iPr_2$)(η^5-$C_5H_4SiMe_3$)$TiCl_2$].

Keeping on mind all these ideas and following our current studies on the chemistry of Cp derivatives of Ti(IV) as precursors for the synthesis of heteronuclear compounds, initially we attempted the preparation of [(η^5-$C_5H_4PPh_2$)(η^5-$C_5H_4SiMe_3$)$TiCl_2$] **1**. Treatment of a solution of [(η^5-$C_5H_4SiMe_3$)$TiCl_3$] in toluene with Tl[$C_5H_4PPh_2$] yielded a 65% of **1** as a brown solid. Further substitution of chloride ligands is achieved upon reaction of **1** with the stoichometric amount of HSPh and slight excess of Et_3N in toluene. Under these conditions the phenylthiolate derivative [(η^5-$C_5H_4PPh_2$)(η^5-$C_5H_4SiMe_3$)$Ti(SPh)_2$] **2** is obtained. As expected, the new compounds **1** and **2** exhibit higher stability in solution when compared with related derivatives [(η^5-$C_5H_4PPh_2$)$_2TiX_2$] (X = Cl, SPh) [11].

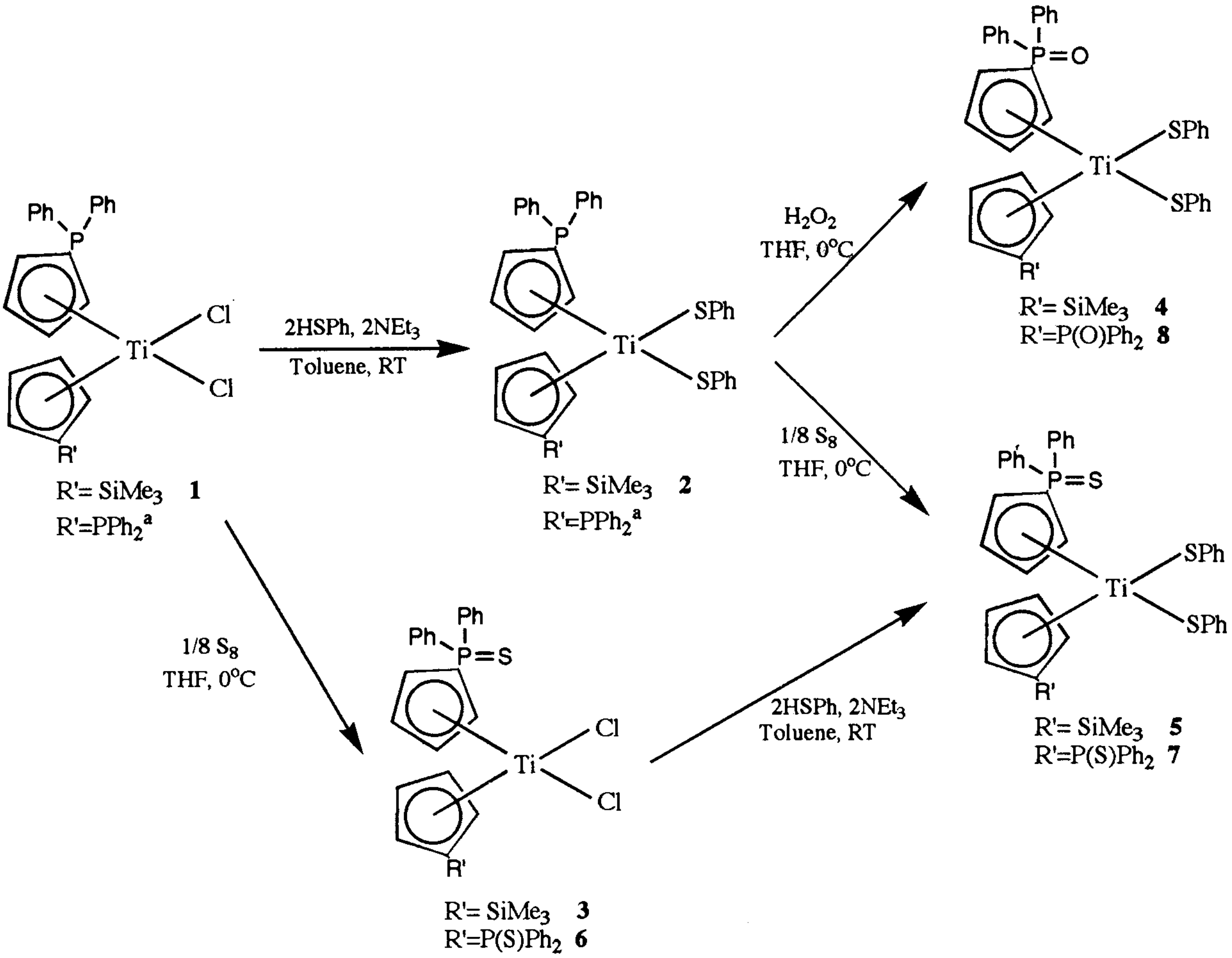
The ^{1}H-NMR spectra show in the Cp region four sets of signals due to the presence of two different monosubstituted Cp rings in the same molecule. The resonances corresponding to $C_5H_4SiMe_3$ and $C_5H_4PPh_2$ appear as two triplets and two multiplets respectively. The assignation of these signals was confirmed on the basis of ^{31}P decoupling in the ^{1}H-NMR spectra of the complexes. The ^{31}P{^{1}H}-NMR spectra exhibit one singlet at − 14.0 ppm for compound **1** and − 15.7 ppm for compound **2**, which are in the same range that related species [(η^5-$C_5H_4PPh_2$)$_2TiX_2$] [11] (X = Cl, SPh).

It is well documented that the P atom in monotertiary phosphines can easily be oxidized to give the corresponding phosphine chalcogenides $R_3P{=}E$ (E = O, S, Se), whose coordination chemistry has been widely explored [8]. A few reports have described the use of 1,1-bis(diphenylphosphoryl)ferrocene as chelate ligand towards Cu, Ag and Au [9]. But as far as we know, nothing has been published on thio- or oxophosphorylcyclopentadienyl titanium complexes. To gain insight into this field we were interested in the synthesis of new mononuclear titanium (IV) complexes using diphenylthio- and diphenyloxophosphorylcyclopentadienyl ligands able to act as precursors to obtain heterobi- or heteropolynuclear compounds.

We have prepared the compounds [(η^5-$C_5H_4P(E)Ph_2$)(η^5-$C_5H_4SiMe_3$)TiX_2] (E = S, X = Cl **3**; E = O, X = SPh **4**; E = S, X = SPh **5**) and [(η^5-$C_5H_4P(E)Ph_2$)$_2TiX_2$] (E = S, X = Cl **6**; E = S, X = SPh **7**; E = O, X = SPh **8**) by reaction of [(η^5-$C_5H_4PPh_2$)(η^5-$C_5H_4SiMe_3$)TiX_2] or [(η^5-$C_5H_4PPh_2$)$_2TiX_2$] (X = Cl, SPh) with the appropriate oxidizer (S_8 or H_2O_2) at 0°C and using toluene or THF as solvent. Orange–red solutions are characteristic of dichloride derivatives **3** and **6**, whereas for the phenylthiolate derivatives **4**, **5**, **7** and **8** deep emerald-green solutions are obtained in all the cases.

When toluene solutions of **3** and **6** are treated with the stoichometric amount of HSC_6H_5 and NEt_3 compounds **5** and **7** are also isolated, nevertheless these reactions have proved to proceed in a much lower yield. All the efforts we made to prepare the analogous bis(chloride) derivatives containing the diphenyloxophosphorylcyclopentadienyl ligand failed (Scheme 1).

The ^{1}H-NMR spectra of these compounds in the Cp region exhibit two sets of signals for each different substituted Cp ring, with the exception of compound **6** which shows only one quartet signal. Again ^{1}H-NMR spectra decoupled from ^{31}P were recorded in order to assign unambiguosly the signals corresponding to the protons of the rings. The presence of $Ph_2P{=}E$ (E = O, S), a relatively more electronegative group than Ph_2P, may cause a higher deshielding in the Cp ring and consequently provoke a downfield shift for these protons. Furthermore, as we mentioned before the lower electronegativity of SPh comparing to that of chloride



Scheme 1. Synthetic route to complexes **2**–**8**. [a] Taken from ref. [11].

ligand should shift the resonances of Cp protons to upfield. The ^{1}H-NMR spectra recorded point out that both effects are taking place.

Upon oxidation or sulfurization of the (diphenylphosphino)cyclopentadienyl group the ^{31}P chemical shifts of compounds **3**–**8** move to downfield, as expected, consistent with a change from P(III) to P(V).

In the IR spectra the stretching vibration frequencies of P=E (E = O, S) appear in the normal range for these groups [13]. The mass spectra show the molecular ion peaks. Fragments attributable to $[M^+ - X]$ and $[M^+ - 2X]$ (X = Cl, SPh) are prominent in all the cases.

2.1. Crystal structure of $[(\eta^5\text{-}C_5H_4P(S)Ph_2)(\eta^5\text{-}C_5H_4SiMe_3)TiCl_2]$ (3)

The molecular structure showing the atom numbering scheme is presented in Fig. 1. Crystal data for complexes **3** and **7** are given in Table 1, while selected bond lengths and angles for **3** are listed in Table 2. The complex shows a distorted tetrahedral arrangement about the titanium atom made up of the two chlorides and the two centroids of the diphenylthiophosphoryl- and trimethylsilylcyclopentadienyl ligands. The Ti–Cl distances [2.350(1) and 2.318(1) Å] and Cl–Ti–Cl angle [95.74(5)°] are similar to those found in related compounds $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Ph_5)TiCl_2]$ [14] and $[(\eta^5\text{-}C_5H_4CH_2CH_2N^iPr_2)(\eta^5\text{-}C_5H_4SiMe_3)TiCl_2]$ [7]. As expected for this type of compound, the two substituted Cp rings adopt a ‘staggered’ conformation being positioned the bulky substituents as far as possible. The P=S distance [1.944(2) Å] for the thiophosphorylcyclopentadienyl ligand is in agreement with values previously reported ([8]a, [9]).

2.2. Crystal structure of $[(\eta^5\text{-}C_5H_4P(S)Ph_2)_2Ti(SPh)_2]\cdot C_4H_{10}O$ (7)

An ORTEP illustration of the molecular structure and atom labeling scheme for compound **7** is shown in Fig. 2. Selected bond lengths and angles for **7** are given in Table 3. Theoretical studies and X-ray data [4] found in the literature on relationship between the S(1)–Ti–S(2) angle value and the type of conformer that the thiolate derivatives of biscyclopentadienyl Ti(IV) show

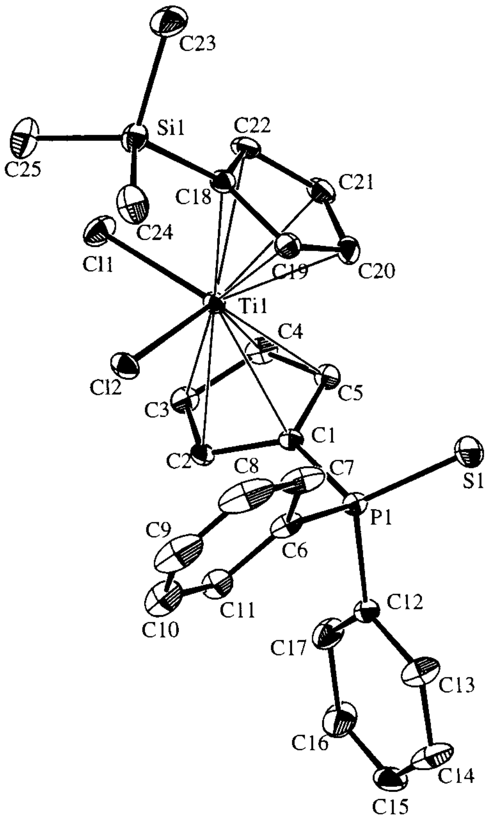


Fig. 1. X-ray structure of compound **3**.

is in agreement with the value of S(1)–Ti–S(2) angle [99.26(7)°] and the *endo* (*anti*) conformation exhibited by the new compound $[(\eta^5\text{-}C_5H_4P(S)Ph_2)_2Ti(SPh)_2]$. Previously we reported [12] a similar behavior for the complex $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(SC_6F_5)_2]$. The geometry at the titanium atom is pseudo-tetrahedral; the Ti–S distances [2.410(2) and 2.423(2) Å] and S(1)–Ti–S(2) [99.26(7)°] are similar to those observed in analogous derivatives [12,15]. A projection of the Cp rings onto the plane formed by the titanium and the two sulfur atoms reveals a 'staggered' conformation for them. The distances of 1.944(2) and 1.942(2) Å for P(1)–S(3) and P(2)–S(4) bonds are comparable to that of compound **3**.

3. Experimental

All the reactions were carried out under argon using Schlenk techniques [16]. Solvents were purified according to standard procedures [17]. The starting materials $Tl[C_5H_4PPh_2]$ [18], $[(\eta^5\text{-}C_5H_4SiMe_3)TiCl_3]$ [19], $[(\eta^5\text{-}C_5H_4PPh_2)_2TiCl_2]$ [11] and $[(\eta^5\text{-}C_5H_4PPh_2)_2Ti(SC_6H_5)_2]$ [11] were prepared as previously described. All the other reagents are commercially available and were used as purchased. IR spectra were recorded on a Perkin Elmer 1650 FT spectrophotometer using KBr pellets. ^1H- and ^{31}P-NMR were recorded on a Bruker AMX-300 and Varian Unity 500 Plus. Chemical shifts are reported in parts per million relative to external standards (TMS for ^1H and 85% H_3PO_4 for ^{31}P). Elemental analyses for C and H were performed with a Perkin-Elmer 2400. FAB positive ion mass spectra were measured on a VG Autospec spectrometer.

3.1. *$[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_4SiMe_3)TiCl_2]$ (**1**)*

$Tl[C_5H_4PPh_2]$ (1.0 g, 2.2 mmol) was added to a solution of $[(\eta^5\text{-}C_5H_4SiMe_3)TiCl_3]$ (0.40 g, 1.4 mmol) in toluene (20 cm^3). After 1 h stirring at room temperature (r.t.) the resultant solution was evaporated to dryness. The solid obtained was extracted with 2 × 5 cm^3 portions of dichloromethane and filtered through a plug of Celite. Removal of the solvent yielded the product as a brown solid. Recrystallization in dichloromethane–hexane (1:2.5) at −20°C afforded analytical pure samples (0.46 g, 65%). Anal. Found: C 59.05, H 5.34. $C_{25}H_{27}Cl_2PSiTi$ requires: C 59.42, H 5.39%. ^1H-NMR ($CDCl_3$): 7.42–7.34 (10H, m, $P\underline{Ph}$), 6.78 (2H, t, $C_5\underline{H}_4SiMe_3$), 6.57 (2H, m, $C_5\underline{H}_4PPh_2$), 6.55 (2H, m, $C_5\underline{H}_4PPh_2$), 6.40 (2H, t, $C_5\underline{H}_4SiMe_3$), 0.27 (9H, s, $Si\underline{Me}$) ppm. $^{31}P\{^1H\}$-NMR ($CDCl_3$): −14.0 (s, $\underline{P}Ph$) ppm. MS: m/z 505 (M^+), 469 ($M^+ - Cl$).

Table 1
Crystallographic data for complexes **3** and **7**

	3	**7**
Empirical formula	$C_{25}H_{25}Cl_2PSSiTi$	$C_{46}H_{38}P_2S_4Ti \cdot C_4H_{10}O$
M_W	535.37	902.96
Crystal size (mm)	0.24 × 0.18 × 0.20	0.05 × 0.275 × 0.35
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Lattice parameters		
a (Å)	10.504(3)	13.341(1)
b (Å)	11.023(5)	14.055(1)
c (Å)	12.155(5)	25.256(1)
α (°)	72.10(3)	
β (°)	80.35(1)	99.931(4)
γ (°)	72.44(1)	
V (Å^3)	1272.5(9)	4664.7(3)
Z	2	4
$D_{calc.}$ (g cm^{-3})	1.397	1.286
F(000)	552	1888
μ (mm^{-1})	6.674	4.148
$2\theta_{max}$ (°)	60	90
hkl Ranges	0–11, −11–12, −13–13	−1–12, −12–12, −22–23
Reflections measured	3777	8476
Reflections observed [$(I > 2\sigma(I)$]	3667	3693
No. variables	280	490
Goodness of fit on F^2	1.027	1.037
Final R	0.0475	0.068
Final weighted R	0.1368	0.178

Table 2
Selected bond lengths (Å) and angles (°) for complex **3**

Bond lengths (Å)			
Ti(1)–Cl(2)	2.318(1)	Ti–Cp(1)	2.102(1)
Ti(1)–Cl(1)	2.350(1)	Ti–Cp(2)	2.072(1)
S(1)–P(1)	1.944(2)	Mean Si–C (methyl groups)	1.867
P(1)–C(1)	1.797(3)	Mean C–C [Cp(1)]	1.404
P(1)–C(6)	1.805(3)	Mean C–C [Cp(2)]	1.406
P(1)–C(12)	1.809(3)	Mean C–C (benzene rings)	1.378
Bond angles (°)			
Cl(2)–Ti(1)–Cl(1)	95.74(5)	C(24)–Si(1)–C(23)	110.1(2)
C(1)–P(1)–C(6)	107.15(14)	C(25)–Si(1)–C(23)	109.0(2)
C(1)–P(1)–C(12)	105.33(14)	C(24)–Si(1)–C(18)	109.5(2)
C(6)–P(1)–C(12)	103.3(2)	C(25)–Si(1)–C(18)	111.3(2)
C(1)–P(1)–S(1)	113.83(11)	C(23)–Si(1)–C(18)	105.5(2)
C(6)–P(1)–S(1)	114.29(13)	Cp(1)–Ti–Cp(2)	132.00
C(12)–P(1)–S(1)	112.05(12)	Mean C–C–C (Cp rings)	108.0
C(24)–Si(1)–C(25)	111.2(2)	Mean C–C–C (benzene rings)	120.2

Cp(1) refers to the centroid of the ring formed by C1, C2, C3, C4 and C5.

Cp(2) refers to the centroid of the ring formed by C18, C19, C20, C21 and C22.

3.2. *[(η^5-$C_5H_4PPh_2$)(η^5-$C_5H_4SiMe_3$)Ti(SPh)$_2$]* (**2**)

To a solution of [(η^5-$C_5H_4PPh_2$)(η^5-$C_5H_4SiMe_3$)-$TiCl_2$] (0.30 g, 0.7 mmol) in toluene (30 cm^3), HSPh (0.14 cm^3, 1.4 mmol) and NEt_3 (0.27 cm^3, 1.6 mmol) were added. After stirring for 3.5 h at r.t., the resultant violet solution was evaporated to dryness. Further purification by chromatography on a silica column, using hexane–toluene (1:4) as eluent, gave a violet band of **2**. Recrystallization from diethyl ether–pentane (1:1.5) at −20°C afforded a violet crystalline solid (0.20 g, 45%). Anal. Found: C 68.43, H 5.76. $C_{37}H_{37}PS_2SiTi$ requires: C 68.08, H 5.71%. ^{1}H-NMR ($CDCl_3$): 7.45–7.07 (20H, m, $P\underline{Ph}$, $S\underline{Ph}$), 6.28 (2H, t, $C_5\underline{H}_4SiMe_3$), 6.25 (2H, m, $C_5\underline{H}_4PPh_2$), 6.19 (2H, m, $C_5\underline{H}_4PPh_2$), 5.99 (2H, t, $C_5\underline{H}_4SiMe_3$), 0.20 (9H, s, $Si\underline{Me}$) ppm. $^{31}P\{^1H\}$-NMR ($CDCl_3$): −15.7 (s, $\underline{P}Ph$) ppm. MS: *m/z* 652 (M^+), 543 ($M^+ - SPh$), 434 ($M^+ - 2SPh$).

3.3. *[(η^5-$C_5H_4P(S)Ph_2$)(η^5-$C_5H_4SiMe_3$)$TiCl_2$]* (**3**)

An ice-cooled solution of [(η^5-$C_5H_4PPh_2$)(η^5-$C_5H_4SiMe_3$)$TiCl_2$] (0.90 g, 1.77 mmol) in toluene (30 cm^3) was treated with sulfur (0.114 g, 3.54 mmol) and the mixture stirred for 1.5 h. The resultant solution was filtered through a plug of celite and the solvent removed in vacuo. Recrystallization from dichloromethane–hexane (1:1) at −20°C afforded red–orange crystals (0.57 g, 63%) suitable for X-ray diffraction study. Anal. Found: C 55.32, H 5.02. $C_{25}H_{27}Cl_2PSSiTi$ requires: C 55.88, H 5.06%. IR: ν_{max} (cm^{-1}) 657 (P=S). ^{1}H-NMR ($CDCl_3$): 7.65–7.43 (10H, m, $P\underline{Ph}$), 7.17 (2H, q, $C_5\underline{H}_4P(S)Ph_2$), 6.83 (4H, m, $C_5\underline{H}_4SiMe_3$), 6.62 (2H, q, $C_5\underline{H}_4P(S)Ph_2$), 0.25 (9H, s, $Si\underline{Me}$) ppm. $^{31}P\{^1H\}$-NMR ($CDCl_3$): 35.4 (s, $\underline{P}(S)Ph$) ppm. MS: *m/z* 536 (M^+), 501 ($M^+ - Cl$).

3.4. *[(η^5-$C_5H_4P(O)Ph_2$)(η^5-$C_5H_4SiMe_3$)Ti(SPh)$_2$]* (**4**)

An ice-cooled solution of [(η^5-$C_5H_4PPh_2$)(η^5-$C_5H_4SiMe_3$)Ti(SPh)$_2$] (0.35 g, 0.53 mmol) in THF (30 cm^3) was treated with 30% H_2O_2 (0.04 cm^3, 0.53 mmol) and the mixture stirred for 1.5 h. The solvent was removed in vacuo and the solid obtained was purified by chromatography on a silica column using toluene–THF (20:1) as eluent to gave a violet–green band of **4**. Recrystallization from diethyl ether solution at −20°C afforded a deep-green crystalline solid (0.26 g, 75%). Anal. Found: C 66.49, H 5.63. $C_{37}H_{37}OPS_2SiTi$ requires: C 66.45, H 5.58%. IR: ν_{max} (cm^{-1}) 1181 (P=O). ^{1}H-NMR ($CDCl_3$): 7.57–7.07 (20H, m, $P\underline{Ph}$, $S\underline{Ph}$); 6.83 (2H, t, $C_5\underline{H}_4SiMe_3$); 6.32 (4H, br d, $C_5\underline{H}_4P(S)Ph_2$); 6.23 (2H, br s, $C_5\underline{H}_4SiMe_3$); 0.21 (9H, s, $Si\underline{Me}$) ppm. $^{31}P\{^1H\}$-NMR ($CDCl_3$): 23.3 (s, $\underline{P}(O)Ph$) ppm. MS: *m/z* 668 (M^+), 559 ($M^+ -$ SPh), 450 ($M^+ - 2SPh$).

3.5. *[(η^5-$C_5H_4P(S)Ph_2$)(η^5-$C_5H_4SiMe_3$)Ti(SPh)$_2$]* (**5**)

Complex **5** was prepared following the same procedure than **4** but using sulfur. Elution from the silica column with hexane–toluene (1:2) and further recrystallization from diethyl ether–hexane (1:1) at −20°C afforded a deep-green crystalline solid (81%). Anal. Found: C 65.10, H 5.65. $C_{37}H_{37}PS_3SiTi$ requires: C 64.89, H 5.45%. IR: ν_{max} (cm^{-1}) 656 (P=S). ^{1}H-NMR ($CDCl_3$): 7.62–7.08 (20H, m, $P\underline{Ph}$, $S\underline{Ph}$), 6.73 (2H, t, $C_5\underline{H}_4SiMe_3$), 6.46 (2H, q, $C_5\underline{H}_4P(S)Ph_2$), 6.36 (2H, br s, $C_5\underline{H}_4P(S)Ph_2$), 5.92 (2H, br s, $C_5\underline{H}_4SiMe_3$), 0.23 (9H, s, $Si\underline{Me}$) ppm. $^{31}P\{^1H\}$-NMR ($CDCl_3$): 35.7 (s, $\underline{P}(S)Ph$) ppm. MS: *m/z* 683 (M^+), 575 ($M^+ - SPh$), 466 ($M^+ - 2SPh$).

3.6. *[(η^5-$C_5H_4P(S)Ph_2$)$_2$$TiCl_2$]* (**6**)

This compound was obtained following the same procedure as **3** with 55% yield. Anal. Found: C 59.64, H 4.16. $C_{34}H_{28}Cl_2P_2S_2Ti$ requires: C 59.93, H 4.14%. IR: ν_{max} (cm^{-1}) 654 (P=S). ^{1}H-NMR ($CDCl_3$): 7.64–7.39 (20H, m, $P\underline{Ph}$), 6.79 (8H, q, $C_5\underline{H}_4P(S)Ph_2$) ppm. $^{31}P\{^1H\}$-NMR ($CDCl_3$): 35.0 (s, $\underline{P}(S)Ph$) ppm. MS: *m/z* 681 (M^+), 646 ($M^+ - Cl$).

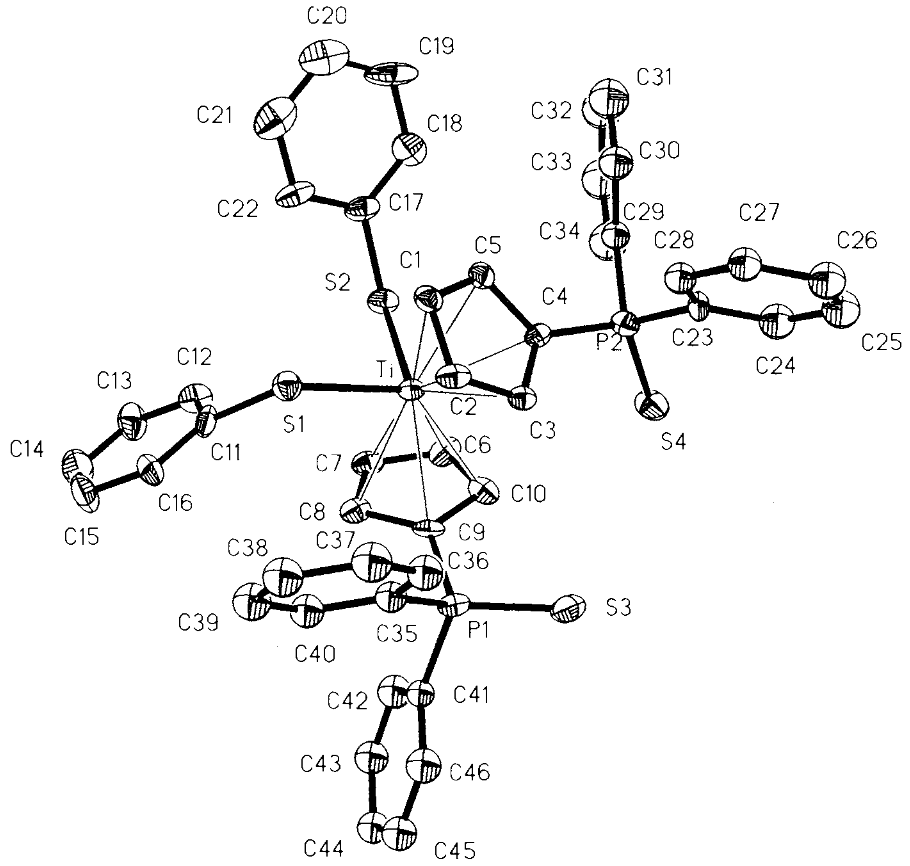


Fig. 2. X-ray structure of compound **7**.

3.7. *[(η^5-$C_5H_4P(S)Ph_2)_2Ti(SPh)_2$] (7)*

An ice-cooled solution of [(η^5-$C_5H_4PPh_2)_2Ti(SPh)_2$] (0.41 g, 0.53 mmol) in THF (30 cm^3) was treated with sulfur (0.034 g, 1.06 mmol) and the mixture stirred for 1.5 h. The solvent was removed in vacuo and the solid obtained washed with hexane leaving the product as a green solid. Recrystallization from diethyl ether solution at -20°C gave deep-green crystals of **7** (80%) suitable for X-ray diffraction study. Anal. Found: C 66.45, H 4.70. $C_{46}H_{38}P_2S_4Ti$ requires: C 66.66, H 4.62%. IR: ν_{max} (cm^{-1}) 654 (P=S). ^{1}H-NMR ($CDCl_3$): 7.59–7.03 (30H, m, P$\underline{\text{Ph}}$, S$\underline{\text{Ph}}$), 6.80 (4H, m, $C_5\underline{H}_4P(S)Ph_2$), 6.38 (4H, m, $C_5\underline{H}_4P(S)Ph_2$) ppm. $^{31}P\{^1H\}$-NMR ($CDCl_3$): 35.5 (s, $\underline{P}$(S)Ph) ppm. MS: m/z 828 (M^+), 719 (M^+ − SPh), 610 (M^+ − 2SPh).

3.8. *[(η^5-$C_5H_4P(O)Ph_2)_2Ti(SPh)_2$] (**8**)*

This compound was obtained following the same procedure as compound **7** but using 30% H_2O_2 (75%). Anal. Found: C 69.07, H 4.76. $C_{46}H_{38}P_2O_2S_2Ti$ requires: C 69.34, H 4.81%. IR: ν_{max} (cm^{-1}) 1167 (P=O). ^{1}H-NMR ($CDCl_3$): 7.58–6.97 (30H, m, P$\underline{\text{Ph}}$, S$\underline{\text{Ph}}$), 6.85 (4H, m, $C_5\underline{H}_4P(O)Ph_2$), 6.53 (4H, br s, $C_5\underline{H}_4P(O)Ph_2$) ppm. $^{31}P\{^1H\}$-NMR ($CDCl_3$): 22.4 (s, $\underline{P}$(O)Ph) ppm. MS: m/z 719 (M^+), 687 (M^+ − SPh), 578 (M^+ − 2SPh).

3.9. *Crystal structure of complex (**3**)*

Suitable crystals for X-ray studies of compound $C_{25}H_{25}Cl_2PSSiTi$ were obtained from dichloromethane/n-hexane at -20°C. A red crystal was mounted in a glass capillary and data were collected on an Enraf-Nonius CAD4 diffractometer, using graphite monochromated Cu–K$_\alpha$ radiation. Crystal data are given in Table 1. No extinction correction was applied. Absorption was corrected using ψ-scan data [20], 1.171 and 0.781 being the maximum and minimum corrections. The structure was solved by direct methods using SIR92 [21] and was refined by LS analysis using SHELX93 [22] with anisotropic parameters for non-H atoms. The positions of the H atoms were refined using the riding model on the corresponding C atoms.

3.10. *Crystal structure of complex (**7**)·$C_4H_{10}O$*

Single crystals of compound $C_{46}H_{38}P_2S_4Ti \cdot C_4H_{10}O$ were grown by cooling a saturated solution of the complex at -20°C. A deep green crystal was selected and mounted on a Siemens P4R diffractometer. Data

Table 3
Selected bond lengths (Å) and angles (°) for complex **7**

Bond lengths (Å)			
Ti(1)–S(1)	2.410(2)	P(1)–C(41)	1.821(6)
Ti(1)–S(2)	2.423(2)	P(2)–C(4)	1.803(6)
S(1)–C(11)	1.765(7)	P(2)–C(23)	1.808(7)
S(2)–C(17)	1.766(7)	P(2)–C(29)	1.805(7)
P(1)–S(3)	1.944(2)	Ti–Cp(1)	2.092
P(2)–S(4)	1.942(2)	Ti–Cp(2)	2.084
P(1)–C(9)	1.819(6)	Mean C–C (Cp rings)	1.402
P(1)–C(35)	1.801(7)	Mean C–C (benzene rings)	1.371
Bond angles (°)			
S(1)–Ti–S(2)	99.26(7)	S(4)–P(2)–C(4)	117.3(2)
Ti(1)–S(1)–C(11)	116.2(2)	S(4)–P(2)–C(23)	112.8(2)
Ti(1)–S(2)–C(17)	112.3(2)	S(4)–P(2)–C(29)	112.0(2)
S(3)–P(1)–C(9)	112.7(2)	C(4)–P(2)–C(23)	100.9(3)
S(3)–P(1)–C(35)	114.2(3)	C(4)–P(2)–C(29)	106.3(3)
S(3)–P(1)–C(41)	112.4(2)	C(23)–P(2)–C(29)	106.6(3)
C(9)–P(1)–C(35)	108.1(3)	Cp(1)–Ti–Cp(2)	135.1
C(9)–P(1)–C(41)	104.5(3)	Mean C–C–C (Cp rings)	108.0
C(35)–P(1)–C(41)	104.2(3)	Mean C–C–C (benzene rings)	120.0

Cp(1) refers to the centroid of the ring formed by C1, C2, C3, C4 and C5.

Cp(2) refers to the centroid of the ring formed by C6, C7, C8, C9 and C10.

were collected using Cu–K_α radiation by the $\omega/2\theta$ technique. Crystal data are given in Table 1. No extinction correction was applied. The structure was solved by direct methods and refined by full matrix least squares technique using the program SHELXTL version 5 [23]. All ring-carbon atoms were founded by differential synthesis but refined as ‘rigid groups’ with the H atoms located by geometric calculations. The rest of the atoms were refined anisotropically. This compound crystallizes with a disordered diethyl ether molecule.

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