Synthesis and characterization of titanium(IV) complexes containing the diphenylphosphino- and diphenylthiophosphoryl-functionalized cyclopentadienyl ligand. Crystal and molecular structure of Ti(η⁵-C₅H₄PPh₂)Cl₃

Juan C. Flores a, Rocío Hernández a, Pascual Royo a, Angelika Butt b, Thomas P. Spaniol b, Jun Okuda b,*

a Departamento de Química Inorgánica, Universidad de Alcalá, Campus Universitario, E-28871 Alcalá de Henares, Spain
b Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg-Universität Mainz, Duesbergweg 10-14, D-55099 Mainz, Germany

Received 4 June 1999; accepted 13 July 1999

Dedicated to Professor Fausto Calderazzo on the occasion of his 70th birthday.

Abstract

The trimethylsilyl cyclopentadiene derivative C₅H₄(SiMe₃)PPh₂ (1) was treated with TiCl₄ to give the air- and moisture-sensitive mono(cyclopentadienyl) compound Ti(η⁵-C₅H₄PPh₂)Cl₃ (4). Reaction of 4 with Mg(CH₂C₆H₅)₂(THF)₂ gave Ti(η⁵-C₅H₄PPh₂)(CH₂C₆H₅)₃ (5). Reactions of the lithium and thallium derivatives M(C₅H₄P(S)Ph₂) (M = Li (2), Ti (3)) with one equiv. of TiCl₄ afforded the mono(cyclopentadienyl) complex Ti(η⁵-C₅H₄P(S)Ph₂)Cl₃ (6), whereas reaction with 0.5 equiv. of TiCl₄ gave the bis(cyclopentadienyl) complex Ti(η⁵-C₅H₄P(S)Ph₂)₂Cl₂ (8). Compound 6 was also isolated as a minor product from the reaction of Ti(η⁵-C₅H₄P(S)Ph₂)₂Cl₂ (8) with one equiv. of TiCl₄. The major product was identified as an inseparable mixture of two compounds [Ti(η⁵-C₅H₄P(S)Ph₂)Cl₂·TiCl₄]n (7a and 7b). Reaction of Ti(η⁵-C₅H₄)Cl₃ with 3 afforded the ‘mixed-ring’ bis(cyclopentadienyl) complex Ti(η⁵-C₅H₄P(S)Ph₂)(η⁵-C₅H₅)Cl₂ (9). Compounds 6–9 are very moisture-sensitive and easily decompose to form the cyclopentadiene C₅H₅P(S)Ph₂. Structural data of these complexes indicate η⁵-coordination of the substituted cyclopentadienyl ligands and this coordination mode was confirmed by X-ray crystal structure analysis of compound 4. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Cyclopentadienyl ligand; Phosphorus; Titanium; Ligand redistribution

1. Introduction

Of the functionalized cyclopentadienyl ligands for transition metal centers [1], those with an intramolecularly coordinated additional donor group [2] have attracted considerable interest recently. Group 4 metal complexes containing one such bidentate ligand are particularly important homogeneous polymerization catalyst precursors [3]. On the other hand, the substituent effects of heteroatom functions directly bonded to the periphery of the cyclopentadienyl ring have not been developed extensively, although the corresponding cyclopentadienies are easily accessible [4]. Such ligands systems are known to form polynuclear complexes by intermolecular coordination to other metal fragments [5]. Therefore we set out to explore the chemistry of titanium(IV) complexes containing the diphenylphosphino- and diphenylthiophosphoryl–cyclopentadienyl ligands. We describe here the synthesis of the new mono(cyclopentadienyl) compounds Ti(η⁵-C₅H₄PPh₂)-Cl₃ and Ti(η⁵-C₅H₄P(S)Ph₂)Cl₃ and the bis(cyclopentadienyl) complexes Ti(η⁵-C₅H₄P(S)Ph₂)₂Cl₂ and Ti(η⁵-C₅H₄P(S)Ph₂)(η⁵-C₅H₅)Cl₂. During the course of this study, the synthesis of several similar complexes was reported independently [6].
2. Results and discussion

Addition of one equiv. of Ph2PCl to Li(C5H5SiMe3) gives the cyclopentadiene C5H4(SiMe3)PPh2 (1) which can be isolated as an orange-yellow oil in high yield (Scheme 1). The product is soluble in hexane and CH2Cl2, and according to its 1H-NMR spectrum it is sufficiently pure to be used in subsequent complexation reactions. The 1H-NMR spectrum contains one broad singlet and two multiplets for the cyclopentadienyl protons indicating the presence of a mixture of isomers. Addition of one equiv. of Li²Bu to C5H5P(S)Ph2 affords compound Li(C5H5P(S)Ph2)2 (2) in quantitative yield (Scheme 1). A THF adduct (ratio THF/Li = 2) of this lithium salt was isolated as a highly air-sensitive foamy yellowish-white solid, soluble in aromatic solvents and THF. This compound was also obtained from the metal exchange reaction of the thallium derivative Ti[C5H5P(S)Ph2] with LiMe (Scheme 1), where the initial formation of the byproduct ‘TlMe’ can be inferred, since its disproportionation products were posed in most instances to insoluble yellow–white powders that could not be characterized. Eventually we succeeded in obtaining 4 as shiny purple crystals suitable for single-crystal X-ray analysis using a CH2Cl2/hexane mixture. The 1H-NMR spectrum of 4 contains two multiplets for the protons on the substituted cyclopentadienyl ring, together with characteristic resonances for the phenyl groups. A singlet is observed at –6.64 ppm in the 13C-NMR spectrum. Reaction of 4 with (C6H5CH2)2Mg(THF)2 in toluene yielded the tribenzyltitanium complex 5 as brown microcrystals. The 1H-NMR spectrum contained one singlet at 3.00 ppm for the TiCH2 protons with the signals for the benzyl groups that could not be characterized. Eventually we succeeded in obtaining the titanium trichloro complex 4 formed as a purple solid, in good yield, by addition of 1 to TiCl4 in CH2Cl2. Recrystallization attempts from a variety of solvents proved difficult because the complex decomposed in most instances to insoluble yellow–white powders that could not be characterized. Eventually we succeeded in obtaining 4 as shiny purple crystals suitable for single-crystal X-ray analysis using a CH2Cl2/hexane mixture. The 1H-NMR spectrum of 4 contains two multiplets for the protons on the substituted cyclopentadienyl ring, together with characteristic resonances for the phenyl groups. A singlet is observed at –6.64 ppm in the 13C-NMR spectrum. Reaction of 4 with (C6H5CH2)2Mg(THF)2 in toluene yielded the tribenzyltitanium complex 5 as brown microcrystals.

The crystal structure of 4 was determined by X-ray diffraction on a single crystal. Fig. 2 shows an ORTEP plot of the molecular structure and Table 1 summarizes selected bond distances and angles. The geometry...
around the metal atom can be described as a pianostool configuration similar to Ti(η^5-C_5H_5)Cl_3 [12a]. The η^5-bonded cyclopentadienyl ring is practically planar with Ti–C bond distances ranging between 2.330(2) and 2.365(2) Å and with C–C bond distances between 1.401(3) and 1.423(2) Å. Only the distance to the carbon atom C(13) bearing the phosphorus appears slightly elongated, but the cyclopentadienyl fragment can be regarded as η^5-coordinated. The distance between the ring centroid and the Ti center is 2.01 Å, similar to the value for Ti(η^5-C_5H_5)Cl_3. The phosphorus atom deviates from the plane formed by the five ring atoms by 0.25 Å and is directed towards the metal atom. The Ti–P distance of 3.525(1) Å, however, excludes a bonding interaction. The phenyl rings attached to the phosphorus atom form angles of 80 and 60° with respect to the plane defined by the cyclopentadienyl ring. The Ti–Cl bond distances as well as the Cl–Ti–Cl angles closely correspond to those of Ti(η^5-C_5H_5)Cl_3 and other related monosubstituted-cyclopentadienyl complexes [12].

Slow addition of either 2 or 3 in toluene, to a toluene solution of TiCl_4 gives the mono(cyclopentadienyl) complex 6 as a yellow-orange oil, soluble in CH_2Cl_2 and toluene (Scheme 2). The moderate solubility of the thallium compound 3 in toluene makes the reaction sensitive to the rate of addition. Fast addition leads to a mixture of 6 and the bis(cyclopentadienyl) compound 8. Conversely, only compound 6 was isolated (65% yield after workup) when the suspension was added in small portions. The higher solubility of the lithium salt allows better control of the addition process, resulting in a higher yield of 6 (ca. 90%). However, because 2 was isolated as a THF adduct, the titanium compound was contaminated with small amounts of TiCl_4(THF)_2. Ligand redistribution was also used to synthesize 6 [12], by treatment of 8 with 1 equiv. of TiCl_4 in warm toluene (Scheme 2). Compound 6 was isolated as the minor product (< 20%) from this reaction, with a mixture of two compounds 7a and 7b as the major products (vide infra).

Compound 6, regardless of the procedure used to prepare it, was invariably isolated as an oil with at least 1 equiv. of toluene present, and is more moisture-sensitive than Ti(η^5-C_5H_5)Cl_3. Attempts to crystallize this compound (washing with alkanes, recrystallization from toluene or from mixtures of solvents), or to remove toluene (high vacuum: 10^-6 mbar, at room temperature or 50°C), all failed. In fact, repeated crystallization gave successive fractions of a yellow solid, and samples of 6 under high vacuum were also converted quantitatively to the same yellow solid. This solid has been characterized as a mixture of compounds 7 (vide infra). The ^1H-NMR spectrum of 6 shows a complicated AA'BB'X spin system for the substituted cyclopentadienyl ring, recorded as two quartets (δ 6.02 and 6.79), together with characteristic resonances for the phenyl groups and toluene protons, and its ^31P{^1H}-NMR spectrum contains one singlet at δ 38.8.
The titanium–cyclopentadienyl bond apparently has a strong 
characteristic of bis(cyclopentadienyl)-dichlorotitanium complexes 
and is used in compounds of very electropositive metals (e.g. 
Ti(C₅H₅)₂Cl₂). The NMR spectra of these compounds contain toluene which persists after exposure to high vacuum. However, in this case, recrystallization from CH₂Cl₂ gives 8 free of solvent. Compounds 8 and 9 are very moisture-sensitive in contrast to the general stability of bis(cyclopentadienyl)-dichlorotitanium complexes (e.g. Ti(C₅H₅)₂Cl₂). The NMR spectra of 8 and 9, with additional signals due to the nonsubstituted five-membered ring in the latter, are fairly similar to that recorded for 6, and are in agreement with the structures proposed in Scheme 2. The C₅H₅P moiety is an AA’BB’X spin system, observed as two quartets at low field in the ¹H-, as three doublets in the ¹³C{¹H}-, and as one singlet in the ³¹P{¹H}-NMR spectra.

It is well documented that trichloro(cyclopentadienyl)titanium complexes are oxophilic species whose Ti–Cl bonds are easily hydrolyzed to give various Ti–O–Ti products depending on the reaction conditions [13]. In contrast, dichlorobis(cyclopentadienyl) titanium complexes are less oxophilic and more resistant to hydrolysis because they are less electron-deficient and are more coordinatively saturated. Indeed, much more severe conditions are usually needed to hydrolyze their Ti–Cl bonds in reactions where the cyclopentadienyl ligands also remain unaffected [14]. This general behavior contrasts with the extreme moisture-sensitivity of the compounds containing the C₅H₅P(S)Ph₂ ligand (i.e. 6–9), since brief exposure to air results in their rapid hydrolysis to re-form the starting compound C₅H₅P(S)Ph₂.

This unusual behavior has been studied in detail by NMR-tube scale experiments for compound 8. The ¹H-NMR spectrum of samples of 8 in C₆D₆, recorded soon after the addition of H₂O (or D₂O) in a 2:1 molar ratio, shows half of the initial 8 unreacted and the resonances corresponding to C₅H₅P(S)Ph₂ (or C₅H₅DP(S)Ph₂) in a 1:2 cyclopentadiene ratio of 1:2 [15]. The titanium–cyclopentadienyl bond apparently has a poor stability towards hydrolysis than that of the Ti–Cl bonds in 8, as evidenced by the 8/cyclopentadiene ratio observed in the spectrum which increases when excess (1:10) of H₂O (or D₂O) is added.

Splitting cyclopentadienyl–transition metal bonds by reaction with protic substances is a reaction typically used in compounds of very electropositive metals (e.g. lanthanide systems) with notable ionic bond character [12c]. The mentioned yellow solid 7 consisting of a mixture of two compounds (7a + 7b) which could not be separated by recrystallization is also sensitive to moisture and the analytical data for the isolated solid is consistent with an empirical formula 8·TiCl₄·toluene.
The 1H- and 31P-NMR spectra of the yellow mixture 7 contain a set of signals corresponding to ligands; the ratio of the C5H4P(S)Ph2 ligands for the two components 7a/7b is around 1:1, although it varies slightly depending on the sample. We propose 7a and 7b to be two compounds with structures containing TiCl4 bridges formed by coordination of the sulfur atoms from two C5H4P(S)Ph2 ligands to titanium (Fig. 3) [17].

Compounds 7a and 7b are formed from the reaction of the bis(cyclopentadienyl) complex 8, or from the mono(cyclopentadienyl) 6, with 1 equiv. of TiCl4. Moreover, the observations described above are consistent with an equilibrium between 6 and 7 in solution, where 7 precipitates due to its lower solubility in toluene. This equilibrium can be explained if the ring substituent leads to a weaker titanium-cyclopentadienyl bond. The lower covalency would reduce the directional constraints of the bond, thus allowing intermolecular ligand redistribution between 6 and 7. There must also be a solvent effect in this equilibrium, since 6 is quantitatively converted into 7, reducing the toluene content of the sample.

3. Conclusions

The cyclopentadiene C5H4(SiMe3)PPh2 (1) reacts with TiCl4 to yield the trichlorotitanium complex 2 which can be alkylated to give the tribenzyl derivative 5. The crystal structure of 4 confirmed the δ5-coordination of the substituted cyclopentadienyl ring. The C5H4P(S)Ph2 ligand give rise to mono- and bis(cyclopentadienyl)titanium complexes 6–9. The common structural feature in these titanium complexes is the δ5-coordination of the substituted cyclopentadienyl ring to the metal center. However, their chemical behavior indicate that the cyclopentadienyl–titanium bond is weaker as a result of ionic bonding contribution caused by the presence of the phosphorus substituent on the ring.

4. Experimental

4.1. General methods

All operations were performed under argon with Schlenk or dry-box techniques. All common chemicals and solvents were purchased from commercial suppliers and purified as described elsewhere [18]. (Trimethylsilylcyclopentadiene) [19], (diphenylthiophosphorylcyclopentadiene) [16], (C6H5CH2)2Mg(THF)2 [20] and Ti(δ5-C5H4Cl)2Cl [9a], were prepared according to literature procedures. NMR spectra were recorded at 25°C on Varian Unity 500+, Varian Unity VXR-300 or Varian Unity 200 NMR spectrometers. Chemical shifts (δ) are reported in ppm referenced to tetramethylsilane for 1H and 13C, and to H3PO4 for 31P. Elemental analyses were performed by the University of Alcalá Microanalytical Laboratories (UCSA) on a Heraeus CHN-O-Rapid- and by the University of Mainz Analytical Laboratory on a Heraeus CHN-Vario EL microanalyzer. Mass spectra were recorded on Hewlett-Packard 5890 and Finnigan 8230 mass spectrometers.

4.2. Preparation of C5H4(SiMe3)(PPh2) (1)

A solution of Ph2PCl (5.9 ml, 32.8 mmol) in hexane (20 ml) was added dropwise, at 0°C, to a suspension of Li(C5H4SiMe3) (94.73 g, 32.8 mmol) in hexane (130 ml). The reaction mixture was slowly warmed to room temperature and stirred overnight. After filtration of lithium chloride and washing the filtered with hexane (20 ml), the filtrate was evaporated, giving 1 as an orange-yellow oil. Yield: 9.98 g (94%). 1H-NMR (200 MHz, CDCl3): δ = 0.04 (s, 9H, SiCH3), 3.07 (m, 0.5H, C5H4), 3.47 (s, 0.5H, C5H4), 6.50 (m, 3H, C5H4), 7.20 (m, 10H, C6H5); MS (70 eV, EI): m/z (%): 322 (24) [M+], 250 (29) [M+–SiMe3], 183 (28) [PPh2+], 73 (100) [SiMe3+].

4.3. Preparation of Li[C5H4P(S)Ph2](THF)2 (2)

A solution of n-butyllithium (4.4 ml, 1.6 M in hexanes) was added dropwise to a THF solution (150 ml) of C5H4P(S)Ph2 (2.00 g, 7.08 mmol) at –78°C. The reaction mixture was allowed to warm to room temperature and stirred for an additional 3 h. The solvent was removed under vacuum, and the resulting yellow oil treated with cold hexane (2 × 30 ml) to give 2 as a foamy yellowish-white solid in quantitative yield. This air-sensitive lithium salt was isolated as an adduct with 2 equiv. of THF as indicated by 1H-NMR. 1H-NMR (200 MHz, C6D6): δ = 1.24 (m, 8H, THF), 3.38 (m, 8H, THF), 6.45 (bd, 4H, 1J(P,H) = 4.5 Hz, C5H4), 7.00–7.10 (m, 6H, C6H5-meta and para), 8.20–8.33 (dm, 4H, 1J(P,H) = 13.2 Hz, C6H5-ortho); 31P{1H}-NMR (121 MHz, C6D6): δ = 41.18 (s).

4.4. Preparation of Ti{(C5H4P(S)Ph2) (3)

A reaction of TlOEt (0.8 ml, 11.33 mmol) with C5H4P(S)Ph2 (3.20 g, 11.33 mmol) was carried out in...
diethyl ether (200 ml) at 0°C. The resulting brown suspension was stirred for 2 h at room temperature. Then, the solvent was separated by filtration and the solid washed with hexane (2 × 30 ml) affording compound 3 as an air-sensitive brown solid. Yield: 5.02 g (92%).

$^{1}$H-NMR (300 MHz, CD$_2$D$_2$): $\delta$ = 6.17 (dt, 2H, J(P,H) = 4.0 Hz, C$_6$H$_5$); 6.48 (dt, 2H, J(P,H) = 4.0 Hz, C$_6$H$_5$); 7.01–7.07 (m, 6H, C$_6$H$_5$-meta and para); 8.18–8.24 (dm, 4H, J(P,H) = 15.0 Hz, C$_6$H$_5$-meta); 9.31 (d, 1H, J(P,C) = 4.7 Hz, C$_6$H$_5$-para); 9.41 (s, 1H, J(P,C) = 7.7 Hz, para-Cl); 9.92 (s, 1H, J(P,C) = 6.1 Hz, meta-Cl); 10.32 (s, 1H, J(P,C) = 9.4 Hz, ortho-Cl); 11.88 Hz, C$_6$H$_5$-Ar); 120.1 (d, J(P,C) = 250 (12) [M$^+$–PPh$_2$–C$_6$H$_5$]; 186 (11) [C$_6$H$_5$TiCH$_2$]); 108 (31) [PC$_6$H$_5$]; Anal. Calc. for C$_{58}$H$_{35}$PTi: C 79.99, H 6.20. Found: C 76.93, H 2.89.

*4.5. Preparation of Ti($\eta^5$-C$_5H_4PPh_2)_2Cl$_3$ (4)*

A solution of 1 (1.97 g, 6.12 mmol) in 15 ml of CH$_2$Cl$_2$ was added dropwise, at −78°C, to a solution of TiCl$_4$ (0.58 ml, 5.27 mmol) in 140 ml of CH$_2$Cl$_2$. The mixture was slowly added to a stirring solution of the bis(cyclopentadienyl) compound (50 ml) at room temperature. After evaporation of the solvent, the crude product was obtained as a purple microcrystalline solid, which was recrystallized from hexane/CH$_2$Cl$_2$ to give purple single crystals. Yield: 2.12 g (86%).

$^{1}$H-NMR (200 MHz, CDC$_1$Cl): $\delta$ = 6.88 (m, 2H, C$_6$H$_5$); 7.01 (m, 2H, C$_6$H$_5$); 7.38 (d, 10H, C$_6$H$_5$); 115.02 (d, 1H, J(P,C) = 102.5 Hz, C$_6$H$_5$-ipso); 111.63 (d, 1H, J(P,C) = 26.3 Hz, C$_6$H$_5$-meta); 131.98 (d, 4J(P,C) = 3.1 Hz, C$_6$H$_5$-para); 132.64 (d, 4J(P,C) = 11.0 Hz, C$_6$H$_5$-ortho); 132.65 (d, 4J(P,C) = 83.6 Hz, C$_6$H$_5$-ipso); 31P($^1$H)-NMR (121 MHz, CD$_2$D$_2$): $\delta$ = 38.75 (s). Anal. Calc. for C$_{58}$H$_{35}$PTi: C 79.99, H 2.90. Found: C 76.93, H 2.89.

*4.6. Preparation of Ti(C$_5$H$_4PPh_2$)(CH$_2$C$_6$H$_5$)$_3$ (5)*

A filtered solution of 4 (428 mg, 1.06 mmol) in 20 ml of toluene was added to a suspension of (C$_5$H$_4$CH$_2$)$_2$Mg(THF)$_2$ (677 mg, 1.93 mmol) in 20 ml of hexane at −78°C. After allowing to warm up to room temperature, the reaction mixture was stirred for 20 h. Filtration and evaporation of the solvent gave a red oily residue which was dissolved in hexane and stored at −35°C to afford brown microcrystals. Yield: 0.22 g (20%).

$^{1}$H-NMR (400 MHz, CD$_2$D$_2$): $\delta$ = 3.00 (s, 6H, TiCH$_3$); 5.64 (m, 2H, C$_6$H$_5$); 5.85 (m, 2H, C$_6$H$_5$); 6.77–7.51 (m, 25H, PC$_6$H$_5$ and CH$_2$C$_6$H$_5$); 11C($^1$H)-NMR (100 MHz, CD$_2$D$_2$): $\delta$ = 93.9 (TiCH$_3$); 120.1 (d, 4J(P,C) = 10.3 Hz, PC$_6$H$_5$-para); 120.5 (CH$_2$C$_6$H$_5$-para), 123.2 (CH$_2$C$_6$H$_5$-meta), 127.2, 128.8 (C$_6$H$_5$); 128.9 (d, 3J(P,C) = 7.7 Hz, PC$_6$H$_5$-meta); 129.5 (d, 4J(P,C) = 3.1 Hz, J(P,C) = 20.5 Hz, C$_6$H$_5$-ortho); 134.7 (d, 4J(P,C) = 21.1 Hz, C$_6$H$_5$-ipso); MS (70 eV, EI): m/z (%): 250 (12) [M$^+$–PPh$_2$–C$_6$H$_5$] 186 (11) [C$_6$H$_5$TiCH$_2$]; 108 (31) [PC$_6$H$_5$]. Anal. Calc. for C$_{58}$H$_{35}$PTi: C 79.99, H 2.90. Found: C 76.93, H 2.89.

*4.7. Preparation of Ti($\eta^5$-C$_5H_4P(S)PPh_2$)$_3Cl$_3 (6)*

*4.7.1. Procedure A*

A suspension of the thallium salt 3 (2.00 g, 4.12 mmol) in toluene (100 ml) was slowly added in small portions, by cannula, to a solution of TiCl$_4$ (0.45 ml, 4.12 mmol) in toluene (50 ml) at −40°C. After stirring overnight at room temperature, the volatiles were evaporated and the residue was extracted into toluene (40 ml) to give 6. Yield: 1.15 g (64%).

*4.7.2. Procedure B*

A solution of the lithium salt 2 (2.04 g, 7.08 mmol) in toluene (50 ml) was added dropwise to another solution of TiCl$_4$ in the same solvent (50 ml) at −40°C. The yellow reaction mixture was allowed to warm gradually to room temperature, stirred for 20 min, and the LiCl byproduct was filtered out. The solvent of the filtrate was then removed under reduced pressure, affording compound 6 (spectroscopic purity 95%) mixed with a small amount of non separable TiCl$_4$(THF)$_2$. Yield: 2.75 g (89%).

*4.7.3. Procedure C*

A solution of TiCl$_4$ (0.07 ml, 0.65 mmol) in toluene (50 ml) was slowly added to a stirring solution of the bis(cyclopentadienyl) compound 8 (0.44 g, 0.65 mmol, vide infra) in toluene (50 ml) at room temperature. After the addition was completed, the reaction mixture was kept at 60°C overnight, then cooled to room temperature and a yellow precipitate (mixtures of compounds 7, vide infra) was filtered out, and the volatiles of the filtrate removed under vacuum to give compound 6. Yield: 0.05 g (18%).

Regardless of the procedure used, compound 6 was obtained as a very moisture-sensitive yellow-orange oil, and both $^1$H-NMR and elemental analyses indicate that it was isolated with 1 equiv. of remaining toluene. $^{1}$H-NMR (300 MHz, CD$_2$D$_2$): $\delta$ = 6.02 (q, 2H, C$_6$H$_5$), 4.79 (q, 2H, C$_6$H$_5$), 6.92–7.05 (m, 6H, C$_6$H$_5$-meta and para), 7.58–7.66 (dm, 4H, 3J(P,H) = 13.9 Hz, C$_6$H$_5$-ortho); 21.1 Hz, C$_6$H$_5$-ipso); 31P($^1$H)-NMR (121 MHz, CD$_2$D$_2$): $\delta$ = 38.82 (s). Anal. Calc. for C$_{58}$H$_{35}$PTi: C 54.62, H 4.20. Found: C 54.20, H 4.10.
4.8. Preparation of [Ti(η^5-C_5H_5)P(S)Ph_2]_2Cl_2·TiCl_4 (7a and 7b)

4.8.1. Procedure A
Following the reaction described in Procedure C to prepare compound 6, the mixture of compounds 7 was separated by filtration as the major product. Yield: 0.39 g (62%).

4.8.2. Procedure B
Samples of compound 6 were kept under high vacuum (10^-6 mbar), at room temperature overnight, converting the oily mono(cyclopentadienyl) compound 31P{1H}-NMR (121 MHz, C_6D_6): 4.8.2.

Crude 8 (spectroscopic purity 90–97%) mixed with a small amount of inseparable TiCl_4(THF)_2, was obtained from the dropwise addition of a solution of 2 in toluene 1/2 equiv. of TiCl_4 in toluene at ~78°C, and work-up of the reaction mixture. Yield: 40–45%.

Problem with the text: the p-value for the F(000) value is 816. However, the F(000) value is typically very low for a crystal of this size, indicating a possible error in the calculation.

4.9. Preparation of Ti(η^5-C_5H_5)P(S)Ph_2]_2Cl_2 (8)
A suspension of the precursor 3 (2.50 g, 5.15 mmol) in toluene (100 ml) was slowly added in small portions to a solution of TiCl_4 (0.45 ml, 4.12 mmol) in toluene (50 ml) at ~78 °C. After the addition, the red solution was allowed to warm to room temperature, followed by stirring for 2 h and filtration of the TiCl byproduct. Concentration of the toluene solution and cooling overnight afforded 8 as a moisture-sensitive red microcrystalline solid, which was recrystallized from toluene.

Yield: 0.63 g (36%). ^1H-NMR (300 MHz, C_6D_6): δ = 6.67 (q, 4H C_6H_4), 7.42 (q, 4H C_6H_4), 6.94–7.02 (m, 12H C_6H_4-meta and para), 7.56–7.66 (dm, 8H C_6H_4-ortho); 31P{1H}-NMR (121 MHz, C_6D_6): δ = 118.64 (d, 1J(P,C) = 87.5 Hz, C_6H_4-ipso), 125.68 (d, J(P,C) = 10.9 Hz, C_6H_4), 129.02 (d, J(P,C) = 10.2 Hz, C_6H_4), 128.58 (d, 3J(P,C) = 13.3 Hz, C_6H_4-meta), 131.68 (d, J(P,C) = 3.1 Hz, C_6H_4-para), 132.20 (d, 2J(P,C) = 10.9 Hz, C_6H_4-ortho), 133.91 (d, 1J(P,C) = 88.3 Hz, C_6H_4-ipso); 39P{1H}-NMR (121 MHz, C_6D_6): δ = 40.59 (s). Anal. Calc. for C_33H_28Cl_2P_2S_2Ti: C 59.93, H 4.14. Found: C 59.57, H 4.16.

Table 2

<table>
<thead>
<tr>
<th>Crystal data and structure refinement for complex Ti(η^5-C_5H_5)P(S)Ph_2]_2Cl_2 (4)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Parameter</strong></td>
</tr>
<tr>
<td>Formula</td>
</tr>
<tr>
<td>Formula weight (g mol^-1)</td>
</tr>
<tr>
<td>Color</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
</tr>
<tr>
<td>System</td>
</tr>
<tr>
<td>Space group</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
</tr>
<tr>
<td>a (Å)</td>
</tr>
<tr>
<td>b (Å)</td>
</tr>
<tr>
<td>c (Å)</td>
</tr>
<tr>
<td>β (°)</td>
</tr>
<tr>
<td>Z</td>
</tr>
<tr>
<td>μ (g cm^-3)</td>
</tr>
<tr>
<td>μ (Mo Kα) (mm^-1)</td>
</tr>
<tr>
<td>Empirical transmission factors</td>
</tr>
<tr>
<td>F(000)</td>
</tr>
<tr>
<td>θ scan range (°)</td>
</tr>
<tr>
<td>Refl. measured</td>
</tr>
<tr>
<td>Indep. refl. obs.</td>
</tr>
<tr>
<td>Final R indices</td>
</tr>
<tr>
<td>Final R indices (all data)</td>
</tr>
<tr>
<td>Goodness-of-fit</td>
</tr>
<tr>
<td>Parameters refined</td>
</tr>
<tr>
<td>Residual density: max., min. (e Å^-3)</td>
</tr>
</tbody>
</table>
4.11. X-ray crystal structure analysis of 4

Crystallographic data are summarized in Table 2. Single crystals of 4 were grown from a CH$_2$Cl$_2$/hexane solution at −35°C. Data sets were obtained at 296 K using an ENRAF-Nonius CAD4 diffractometer (ω-scan mode, monochromatic Mo–K$_\alpha$ radiation, $\lambda = 0.7107$ Å). The reflections were corrected for Lp effects using the program MOLEN [21a] and for absorption using $\psi$-scans. The structure was solved by direct and Fourier difference methods using the program SHELXS-86 [21b]. The refinement was carried out with the program SHELXL93 based on $F^2$ [21c]. Anisotropic thermal parameters were refined for all non-hydrogen atoms. All hydrogen atoms were located and refined in their positions with isotropic thermal parameters.

5. Supplementary information

Further details of the crystal structure determination are available on request from the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-120982. Copies of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-33603 or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

Acknowledgements

We gratefully acknowledge financial support by DG-ICYT (ref. no. PB-97-0776), Iberdrola, and the Fonds der Chemischen Industrie.

References


[7] TP$_3$: black metallic residue, green in flame test; TlMe$_3$: detected by $^1$H-NMR as a broad resonance ($\delta 0.46$, $J_{1,2} = 40$ Hz).


[14] (a) S.A. Giddings, Inorg. Chem. 3 (1964) 684. (b) S.A. Giddings, Inorg. Chem. 6 (1967) 849.

[15] C₅H₅P(S)Ph₂ has been previously described by Mathey et al. [16]. Here we report detailed spectroscopic data for the major isomer (> 80%) in benzene-δ₆ and for the monodeuterated species C₅H₄DP(S)Ph₂. ¹H-¹H decoupling experiments and computer analysis of the spectrum at 500 MHz (g-NMR 3.6 ± 2 Hz for Mac) allowed the following assignments and determination of the corresponding coupling constants: ¹H-NMR (500 MHz, C₆D₆): δ = 3.15 (quintet, 2H, J_ab = 1.5 Hz, J_ac and J_ad = 1.3 Hz, J(P,H) = 1.5 Hz, C₅H₅-Hₐ), 6.10 (m, 1H, J_ab = 1.5 Hz, J_ac = 5.1 Hz, J_ad = 2.0 Hz, J(P,H) = 1.8 Hz, C₅H₅-Hₐ), 6.27 (m, 1H, J_ab = 1.3 Hz, J_ac = 5.1 Hz, J_ad = 1.1 Hz, J(P,H) = 3.5 Hz, C₅H₅-Hₐ), 6.64 (dm, 1H, J_ab = 1.3 Hz, J_ad = 2.0 Hz, J(P,H) = 1.4 Hz, C₅H₅-Hₐ), 6.96–7.03 (m, 6H, C₆H₅-meta and para), 7.79–7.88 (dm, 4H, J(P,H) = 13.5 Hz, C₆H₅-ortho); ³¹P(¹H)-NMR (121 MHz, C δD₆): δ = 39.51 (s, major isomer), 38.44 (s, minor). The ¹H-NMR spectrum of the monodeuterated compound is similar to the one described for C₅H₅P(S)Ph₂, and a remarkable feature is the slightly lower chemical shift for Hₐ (δ = 3.13) which appears as a broader signal (W₁/₂ = 12 Hz).


