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Synthesis and characterization of titanium(IV) complexes containing the diphenylphosphino- and diphenylthiophosphoryl-functionalized cyclopentadienyl ligand. Crystal and molecular structure of Ti(η^5-$C_5H_4PPh_2$)Cl_3

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

Abstract

The trimethylsilyl cyclopentadiene derivative $C_5H_4(SiMe_3)PPh_2$ (**1**) was treated with $TiCl_4$ to give the air- and moisture-sensitive mono(cyclopentadienyl) compound Ti(η^5-$C_5H_4PPh_2$)Cl_3 (**4**). Reaction of **4** with $Mg(CH_2C_6H_5)_2(THF)_2$ gave Ti(η^5-$C_5H_4PPh_2$)$(CH_2C_6H_5)_3$ (**5**). Reactions of the lithium and thallium derivatives M{$C_5H_4P(S)Ph_2$} (M = Li (**2**), Tl (**3**)) with one equiv. of $TiCl_4$ afforded the mono(cyclopentadienyl) complex Ti{η^5-$C_5H_4P(S)Ph_2$}Cl_3 (**6**), whereas reaction with 0.5 equiv. of $TiCl_4$ gave the bis(cyclopentadienyl) complex Ti{η^5-$C_5H_4P(S)Ph_2$}$_2Cl_2$ (**8**). Compound **6** was also isolated as a minor product from the reaction of Ti{η^5-$C_5H_4P(S)Ph_2$}$_2Cl_2$ (**8**) with one equiv. of $TiCl_4$. The major product was identified as an inseparable mixture of two compounds [Ti{η^5-$C_5H_4P(S)Ph_2$}$_2Cl_2$·$TiCl_4$]$_n$ (**7a** and **7b**). Reaction of Ti(η^5-C_5H_5)Cl_3 with **3** afforded the 'mixed-ring' bis(cyclopentadienyl) complex Ti{η^5-$C_5H_4P(S)Ph_2$}(η^5-C_5H_5)Cl_2 (**9**). Compounds **6**–**9** are very moisture-sensitive and easily decompose to form the cyclopentadiene $C_5H_5P(S)Ph_2$. Structural data of these complexes indicate η^5-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 cyclopentadienes 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(η^5-$C_5H_4PPh_2$)-Cl_3 and Ti{η^5-$C_5H_4P(S)Ph_2$}Cl_3 and the bis(cyclopentadienyl) complexes Ti{η^5-$C_5H_4P(S)Ph_2$]$_2Cl_2$ and Ti{η^5-$C_5H_4P(S)Ph_2$](η^5-C_5H_5)Cl_2. During the course of this study, the synthesis of several similar complexes was reported independently [6].

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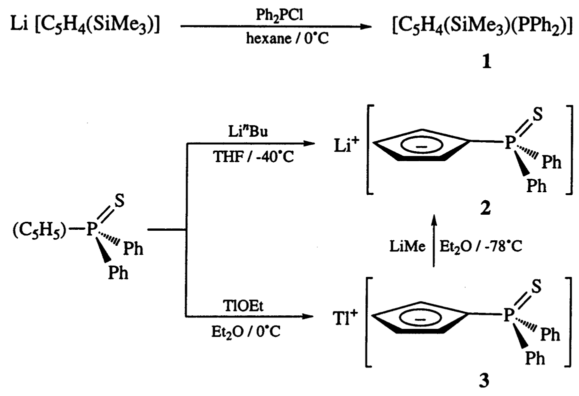


Scheme 1.

2. Results and discussion

Addition of one equiv. of Ph_2PCl to $Li(C_5H_4SiMe_3)$ gives the cyclopentadiene $C_5H_4(SiMe_3)PPh_2$ (**1**) which can be isolated as an orange-yellow oil in high yield (Scheme 1). The product is soluble in hexane and CH_2Cl_2, and according to its ^{1}H-NMR spectrum it is sufficiently pure to be used in subsequent complexation reactions. The ^{1}H-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 Li^nBu to $C_5H_5P(S)Ph_2$ affords compound $Li\{C_5H_4P(S)Ph_2\}$ (**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 $Tl\{C_5H_4P(S)Ph_2\}$ (**3**) with LiMe (Scheme 1), where the initial formation of the byproduct 'TlMe' can be inferred, since its disproportionation products were detected (Tl^0 and $TlMe_3$) [7]. The^{1}H-NMR spectrum of **2** shows a relatively broad virtual doublet (δ 6.45) for the AA'BB'X spin system corresponding to the fragment, with J(P,H) = 4.5 Hz for the four protons. This pattern together with a singlet observed in the $^{31}P\{^1H\}$-NMR spectrum (δ 41.18), indicates that the cyclopentadienyl group of the starting thiophosphoryl compound has been deprotonated.

Reaction of $C_5H_5P(S)Ph_2$ with one equiv. of TlOEt in diethyl ether affords **3** as an air-sensitive brown powder (Scheme 1). Unlike $Tl(C_5H_5)$, compound **3** is soluble enough in aromatic solvents to allow its study by NMR spectroscopy. The NMR data for **3** are also consistent with deprotonation of the cyclopentadienyl ring. The ^{1}H NMR spectrum in C_6D_6 shows the C_5H_4P group as an AA′BB′X spin system (two doublets of virtual triplets at δ 6.17 and 6.48) with J(P,H) = 4.0 Hz for the protons of the ring. The $^{13}C\{^1H\}$-NMR chemical shifts and ^{31}P–^{13}C coupling values of **3** are also within normal ranges for cyclopentadienyl carbons (see Section 4); one singlet appears in its $^{31}P\{^1H\}$ NMR spectrum (δ 38.75). The presence of ^{1}H– and ^{13}C–^{203,205}Tl coupling constants for soluble substituted (cyclopentadienyl)thallium compounds has been attributed to the enforced covalency of the metal–ring interaction in the compound [8]. The absence of ^{1}H, ^{13}C and ^{31}P couplings with ^{203,205}Tl in the spectra of compound **3** may indicate that the interaction in **3** is predominantly ionic in character. The two resonance structures for the anion $[C_5H_4P(S)Ph_2]^-$, shown in Fig. 1, might help to delocalize negative charge to the ligand, thus encouraging ionic bonding in the thallium complex.

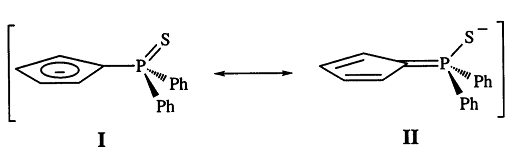


Fig. 1. Resonance structures for the$[C_5H_4P(S)Ph_2]^-$.

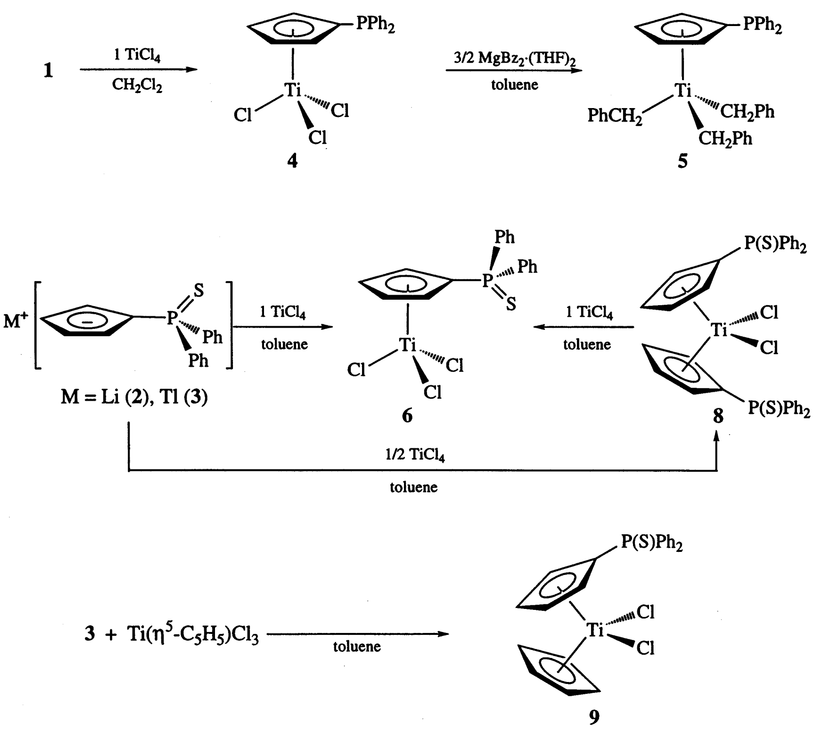
Several approaches have proved useful for the synthesis of group 4 mono- and bis(cyclopentadienyl) chloro complexes. For example, the reaction of $TiCl_4$ with trimethylsilylcyclopentadienes is an efficient method for the synthesis of mono(cyclopentadienyl) complexes [9]. Further reaction of the mono(cyclopentadienyl) complex with a thallium derivative of a different cyclopentadienyl ligand affords 'mixed-ring' titanium compounds [10]. However, the reaction of $TiCl_4$ with two equiv. of an alkali metal cyclopentadienyl salt is the most commonly used procedure for the synthesis of dichlorobis(cyclopentadienyl)titanium complexes [11]. Thus, compounds **4**, **6**, **8**, and **9** were readily prepared from precursors **1**–**3** (Scheme 2).

The titanium trichloro complex **4** was formed as a purple solid, in good yield, by addition of **1** to $TiCl_4$ in CH_2Cl_2. 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 CH_2Cl_2/hexane mixture. The ^{1}H-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 ^{31}P-NMR spectrum. Reaction of **4** with $(C_6H_5CH_2)_2Mg(THF)_2$ in toluene yielded the tribenzyltitanium complex **5** as brown microcrystals. The ^{1}H-NMR spectrum contained one singlet at 3.00 ppm for the $TiCH_2$ protons with the signals for the cyclopentadienyl protons shifted significantly upfield.

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 piano-stool 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 ^{1}H-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 $^{31}P\{^1H\}$-NMR spectrum contains one singlet at δ 38.8.



Scheme 2.

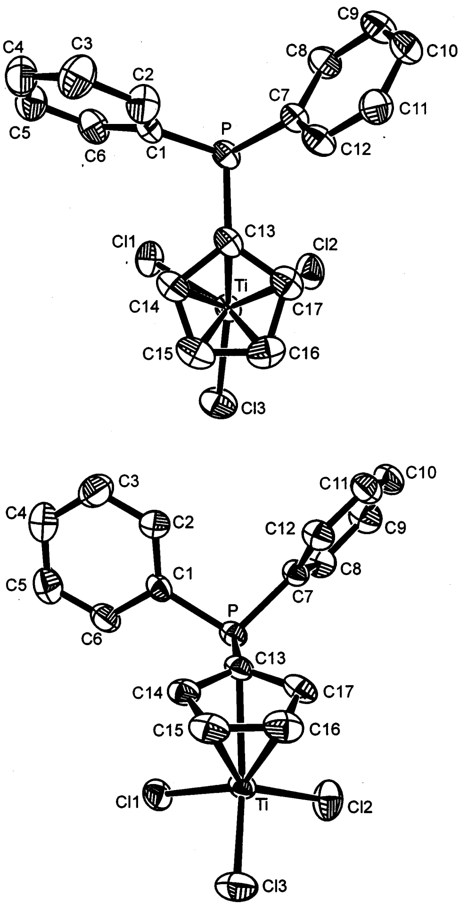


Fig. 2. ORTEP diagram of the molecular structure of Ti(η^5-$C_5H_4PPh_2$)Cl_3 (**4**). Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for the sake of clarity.

Reaction of **3** (or **2**) with $TiCl_4$ in a 2:1 molar ratio in toluene affords the bis(cyclopentadienyl) compound **8** (Scheme 2), while treatment of Ti(η^5-C_5H_5)Cl_3 with 1 equiv. of **3** gives the "mixed-ring" bis(cyclopentadienyl) **9**; both **8** and **9** were obtained as red microcrystalline solids. Again, the purification of **8** proceeds more smoothly when **3** is used as cyclopentadienyl transfer reagent, since $TiCl_4(THF)_2$ is also formed in the reaction of **2** with $TiCl_4$, and this has been found to be difficult to separate. Solid samples of compound **8** contain toluene which persists after exposure to high vacuum. However, in this case, recrystallization from CH_2Cl_2 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. $Ti(C_5H_5)_2Cl_2$). 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 C_5H_4P moiety is an AA′BB′X spin system, observed as two quartets at low field in the ^1H-, as three doublets in the $^{13}C\{^1H\}$-, and as one singlet in the $^{31}P\{^1H\}$-NMR spectra.

Table 1
Selected bond lengths (Å) and angles (°) for Ti(η^5-$C_5H_4PPh_2$)Cl_3 (**4**)

Bond lenghts		Bond angles	
Ti–Cl(1)	2.2427(8)	Cl(2)–Ti–Cl(3)	102.65(3)
Ti–Cl(2)	2.2225(8)	Cl(2)–Ti–Cl(1)	104.57(3)
Ti–Cl(3)	2.2318(9)	Cl(3)–Ti–Cl(1)	101.72(3)
Ti–C(13)	2.365(2)	C(7)–P–C(13)	102.55(7)
Ti–C(14)	2.339(2)	C(7)–P–C(1)	103.76(8)
Ti–C(15)	2.330(2)	C(13)–P–C(1)	100.48(7)
Ti–C(16)	2.335(2)		
Ti–C(17)	2.347(2)		
P–C(1)	1.839(2)		
P–C(7)	1.822(2)		
P–C(13)	1.830 (2)		
C(13)–C(14)	1.418(2)		
C(13)–C(17)	1.423(2)		
C(14)–C(15)	1.404(2)		
C(15)–C(16)	1.401(3)		
C(16)–C(17)	1.407(3)		

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 $C_5H_4P(S)Ph_2$ ligand (i.e. **6**–**9**), since brief exposure to air results in their rapid hydrolysis to re-form the starting compound $C_5H_5P(S)Ph_2$.

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 C_6D_6, recorded soon after the addition of H_2O (or D_2O) in a 2:1 molar ratio, shows half of the initial **8** unreacted and the resonances corresponding to $C_5H_5P(S)Ph_2$ (or $C_5H_4DP(S)Ph_2$) in a **8**/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 H_2O (or D_2O) 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**·$TiCl_4$·toluene.

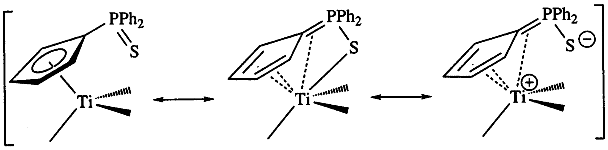


Fig. 3. Resonance structures proposed for a [Ti($C_5H_4P(S)Ph_2$)] moiety.

The ^{1}H- and ^{31}P-NMR spectra of the yellow mixture **7** contain a set of signals corresponding to ligands; the ratio of the $C_5H_4P(S)Ph_2$ 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 $TiCl_4$ bridges formed by coordination of the sulfur atoms from two $C_5H_4P(S)Ph_2$ 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 $TiCl_4$. 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 $C_5H_4(SiMe_3)PPh_2$ (**1**) reacts with $TiCl_4$ to yield the trichlorotitanium complex **2** which can be alkylated to give the tribenzyl derivative **5**. The crystal structure of **4** confirmed the η^5-coordination of the substituted cyclopentadienyl ring. The $C_5H_4P(S)Ph_2$ ligand give rise to mono- and bis(cyclopentadienyl)titanium complexes **6**–**9**. The common structural feature in these titanium complexes is the η^5-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]. (Trimethylsilyl)cyclopentadiene [19], (diphenylthiophosphoryl)cyclopentadiene [16], $(C_6H_5CH_2)_2Mg(THF)_2$ [20] and Ti(η^5-C_5H_5)Cl_3 [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 ^{1}H and ^{13}C, and to H_3PO_4 for ^{31}P. 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 $C_5H_4(SiMe_3)(PPh_2)$ (1)

A solution of Ph_2PCl (5.9 ml, 32.8 mmol) in hexane (20 ml) was added dropwise, at 0°C, to a suspension of Li($C_5H_4SiMe_3$) (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 filterbed with hexane (20 ml), the filtrate was evaporated, giving **1** as an orange-yellow oil. Yield: 9.98 g (94%). ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = -0.04$ (s, 9H, $SiCH_3$), 3.07 (m, 0.5H, C_5H_4), 3.47 (s, 0.5H, C_5H_4), 6.50 (m, 3H, C_5H_4), 7.20 (m, 10H, C_6H_5); MS (70 eV, EI): m/z (%) = 322 (24) [M^+], 250 (29) [M^+–$SiMe_3$], 183 (28) [PPh_2^+], 73 (100) [$SiMe_3^+$].

4.3. Preparation of Li{$C_5H_4P(S)Ph_2$}$(THF)_2$ (2)

A solution of *n*-butyllithium (4.4 ml, 1.6 M in hexanes) was added dropwise to a THF solution (150 ml) of $C_5H_5P(S)Ph_2$ (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 ^{1}H-NMR. ^{1}H-NMR (200 MHz, C_6D_6): $\delta = 1.24$ (m, 8H, THF), 3.38 (m, 8H, THF), 6.45 (bd, 4H, $^1J(P,H) = 4.5$ Hz, C_5H_4), 7.00–7.10 (m, 6H, C_6H_5-*meta and para*), 8.20–8.33 (dm, 4H, $^3J(P,H) = 13.2$ Hz, C_6H_5-*ortho*); $^{31}P\{^1H\}$-NMR (121 MHz, C_6D_6): $\delta = 41.18$ (s).

4.4. Preparation of Tl{(C_5H_4)P(S)Ph_2} (3)

A reaction of TlOEt (0.8 ml, 11.33 mmol) with $C_5H_5P(S)Ph_2$ (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, C_6D_6): $\delta = 6.17$ (dt, 2H, J(P,H) = 4.0 Hz, C_5H_4), 6.48 (dt, 2H, J(P,H) = 4.0 Hz, C_5H_4), 7.01–7.07 (m, 6H, C_6H_5-*meta* and *para*), 8.18–8.24 (dm, 4H, ^3J(P,H) = 15.0 Hz, C_6H_5-*ortho*); ^{13}C{^{1}H}-NMR (75 MHz, C_6D_6): $\delta = 111.63$ (d, J(P,C) = 15.2 Hz, C_5H_4), 115.02 (d, ^1J(P,C) = 102.5 Hz, C_5H_4-*ipso*), 115.69 (d, J(P,C) = 14.0 Hz, C_5H_4), 128.19 (d, ^3J(P,C) = 26.3 Hz, C_6H_5-*meta*), 131.98 (d, ^4J(P,C) = 3.1 Hz, C_6H_5-*para*), 132.64 (d, ^2J(P,C) = 11.0 Hz, C_6H_5-*ortho*), 132.65 (d, ^1J(P,C) = 83.6 Hz, C_6H_5-*ipso*); ^{31}P{^{1}H}-NMR (121 MHz, C_6D_6): $\delta = 38.75$ (s). Anal. Calc. for $C_{17}H_{14}PSTl$: C 42.04, H 2.90. Found: C 41.48, H 2.89.

4.5. Preparation of *Ti(η^5-C$_5$H$_4$PPh$_2$)Cl$_3$ (4)*

A solution of **1** (1.97 g, 6.12 mmol) in 15 ml of CH_2Cl_2 was added dropwise, at −78°C, to a solution of $TiCl_4$ (0.58 ml, 5.27 mmol) in 140 ml of CH_2Cl_2. The solution immediately turned to a purple color. It was warmed slowly to room temperature and stirred overnight. After evaporation of the solvent, the crude product was obtained as a purple microcrystalline solid, which was recrystallized from hexane/CH_2Cl_2 to give purple single crystals. Yield: 2.12 g (86%). ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 6.88$ (m, 2 H, C_5H_4), 7.01 (m, 2 H, C_5H_4), 7.38 (d, 10 H, C_6H_5); ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): $\delta = 125.1$ (s, C_5H_4), 126.4 (d, ^4J(P,C) = 8.25 Hz, C_6H_5-*para*), 128.9 (d, ^3J(P,C) = 7.75 Hz, C_6H_5-*meta*), 129.9 (s, C_5H_4), 134.1 (d, ^2J(P,C) = 23.88 Hz, C_6H_5-*ortho*), 134.80 (d, ^1J(P,C) = 11.88 Hz, C_6H_5-*ipso*), 142.5 (d, ^1J(P,C) = 25.38 Hz, C_5H_4-*ipso*); ^{31}P{^{1}H}-NMR (121 MHz, C_6D_6): $\delta = 6.64$ (s). Anal. Calc. for $C_{17}H_{14}Cl_3PTi$: C 50.75, H 3.51. Found: C 52.07, H, 3.83.

4.6. Preparation of *Ti(C$_5$H$_4$PPh$_2$)(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 $(C_6H_5CH_2)_2Mg(THF)_2$ (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, C_6D_6): $\delta = 3.00$ (s, 6 H, $TiCH_2$), 5.64 (m, 2 H, C_5H_4), 5.85 (m, 2 H, C_5H_4), 6.77–7.51 (m, 25 H, PC_6H_5 and $CH_2C_6H_5$); ^{13}C{^{1}H}-NMR (100 MHz, C_6D_6): $\delta = 93.9$ ($TiCH_2$), 120.1 (d, ^4J(P,C) = 10.3 Hz, PC_6H_5-*para*), 120.5 ($CH_2C_6H_5$-*para*), 123.2 ($CH_2C_6H_5$-*meta*), 127.2, 128.8 (C_5H_4), 128.9 (d, ^3J(P,C) = 7.7 Hz, PC_6H_5-*meta*), 129.5 ($CH_2C_6H_5$-*ortho*), 134.2 (d, ^1J(P,C) = 20.5 Hz, C_5H_4-*ipso*), 134.7 (d, ^2J(P,C) = 21.1 Hz, PC_6H_5-*ortho*), 137.9 (d, ^1J(P,C) = 11.0 Hz, PC_6H_5-*ipso*), 148.6 ($CH_2C_6H_5$-*ipso*); MS (70 eV, EI): m/z (%) = 250 (12) [M^+–PPh_2, –$2C_7H_7$], 186 (11) [$C_5H_4TiCH_2^+$], 108 (31) [$PC_6H_6^+$]. Anal. Calc. for $C_{38}H_{35}PTi$: C 79.99, H 6.20. Found: C 76.93, H 5.82.

4.7. Preparation of *Ti{η^5-C$_5$H$_4$P(S)Ph$_2$}Cl$_3$ (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, C_6D_6): $\delta = 6.02$ (q, 2H, C_5H_4), 6.79 (q, 2H, C_5H_4), 6.92–7.05 (m, 6H, C_6H_5-*meta* and *para*), 7.58–7.66 (dm, 4H, ^3J(P,H) = 13.9 Hz, C_6H_5-*ortho*); ^{31}P{^{1}H}-NMR (121 MHz, C_6D_6): $\delta = 38.82$ (s). Anal. Calc. for $C_{17}H_{14}Cl_3PSTi \cdot C_7H_8$: C 54.62, H 4.20. Found: C 54.20, H 4.10.

4.8. Preparation of *[Ti{(η^5-C_5H_4)P(S)Ph_2}$_2Cl_2$·$TiCl_4$]$_n$ (**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 into the mixture **7**. Yield: quantitative.

In addition, attempts to crystallize compound **6** all failed (toluene, toluene/CH_2Cl_2 or hexane/toluene), instead, they resulted in the separation of several crops of **7**. The mixture **7** was obtained as a moisture-sensitive yellow microcrystalline solid. ^{1}H-NMR and elemental analysis indicate the presence of toluene in the mixture, according to a general formula [Ti{(η^5-C_5H_4)P(S)Ph_2}$_2Cl_2$·($TiCl_4$)·toluene]$_n$ This composition was unchanged when the solid was kept under high vacuum (10^{-6} mbar) overnight at 50°C. ^{1}H-NMR (300 MHz, C_6D_6): $\delta = 6.19$ (q, 2H, C_5H_4–**7a**), 6.24 (q, 2H, C_5H_4–**7a**), 6.55 (q, 2H, C_5H_4–**7b**), 6.94 (q, 2H, C_5H_4–**7b**), 6.96–7.04 (m, 6H + 6H, C_6H_5-*meta* and *para*-**7a** and **7b**), 7.37–7.46 (dm, 4H, ^3J(P,H) = 13.5 Hz, C_6H_5-*ortho*-**7a**), 7.66–7.74 (m, 4H, C_6H_5-*ortho*-**7b**); ^{31}P{^{1}H}-NMR (121 MHz, C_6D_6): $\delta = 39.06$ (s, **7a**), 39.16 (s, **7b**). Anal. Calc. for $C_{34}H_{28}Cl_6P_2S_2Ti_2$·$C_7H_8$: C 50.86, H 3.91. Found: C 51.12, H 3.77.

4.9. Preparation of *Ti{η^5-C_5H_4P(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 TlCl 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%). ^{1}H-NMR (300 MHz, C_6D_6): $\delta =$ 6.67 (q, 4H C_5H_4), 7.42 (q, 4H C_5H_4), 6.94–7.02 (m, 12H C_6H_5-*meta* and *para*), 7.56–7.66 (dm, 8H ^3J(P,H) = 13.6 Hz, C_6H_5-*ortho*); ^{13}C{^{1}H}-NMR (125 MHz, C_6D_6): $\delta = 118.64$ (d, ^1J(P,C) = 87.5 Hz, C_5H_4-*ipso*), 125.68 (d, J(P,C) = 10.9 Hz, C_5H_4), 129.02 (d, J(P,C) = 10.2 Hz, C_5H_4), 128.58 (d, ^3J(P,C) = 13.3 Hz, C_6H_5-*meta*), 131.68 (d, J(P,C) = 3.1 Hz, C_6H_5-*para*), 132.20 (d, ^2J(P,C) = 10.9 Hz, C_6H_5-*ortho*), 133.91 (d, ^1J(P,C) = 88.3 Hz, C_6H_5-*ipso*); ^{31}P{^{1}H}-NMR (121 MHz, C_6D_6): $\delta = 40.59$ (s). Anal. Calc. for $C_{34}H_{28}Cl_2P_2S_2Ti$: C 59.93, H 4.14. Found: C 59.57, H 4.16.

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 to 1/2 equiv. of $TiCl_4$ in toluene at −78°C, and work-up of the reaction mixture. Yield: 40–45%.

4.10. Preparation of *Ti{η^5-C_5H_4P(S)Ph_2}(η^5-C_5H_5)Cl_2 (**9**)*

A mixture of Ti(η^5-C_5H_5)Cl_3 (0.58 g, 2.65 mmol) and **3** (1.30 g, 2.65 mmol) was warmed up to 60°C in toluene (100 ml) and stirred overnight. After filtration of the precipitate (TlCl), the red solution was concentrated and cooled at −30°C for 24 h to give compound **9** as a moisture-sensitive red microcrystalline solid. This product was recrystallized from CH_2Cl_2. Yield: 0.68 g (55%). ^{1}H-NMR (300 MHz, C_6D_6): $\delta = 6.22$ (q, 2H C_5H_4), 6.71 (q, 2H C_5H_4), 6.43 (s, 5H C_5H_5), 6.96–7.02 (m, 6H C_6H_5-*meta* and *para*), 7.54–7.63 (dm, 8H ^3J(P,H) = 13.6 Hz, C_6H_5-*ortho*); ^{13}C{^{1}H}-NMR (75 MHz, C_6D_6): $\delta = 115.13$ (d, ^1J(P,C) = 86.3 Hz, C_5H_4-*ipso*), 122.27 (s, C_5H_5), 123.28 (d, J(P,C) = 10.1 Hz, C_5H_4), 126.85 (d, J(P,C) = 10.1 Hz, C_5H_4), 128.51 (d, ^3J(P,C) = 12.8 Hz, C_6H_5-*meta*), 131.72 (bs, C_6H_5-*para*), 132.20 (d, ^2J(P,C) = 11.9 Hz, C_6H_5-*ortho*), 133.97 (d, ^1J(P,C) = 87.9 Hz, C_6H_5-*ipso*); ^{31}P{^{1}H}-NMR (121

Table 2
Crystal data and structure refinement for complex Ti(η^5-$C_5H_4PPh_2$)Cl_3 (**4**).

Formula	$C_{17}H_{14}Cl_3PTi$
Formula weight (g mol^{-1})	403.50
Crystal color	Purple
Crystal size (mm)	0.63 × 0.45 × 0.38
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
Unit cell dimensions	
a (Å)	10.629(4)
b (Å)	6.484(2)
c (Å)	25.169(8)
β (°)	92.45(3)
Z	4
$\rho_{calc.}$ (g cm^{-3})	1.547
μ(Mo–K$_\alpha$) (mm^{-1})	1.04
Empirical transmission factors	90.25 – 99.99 %
F(000)	816
θ scan range (°)	30
T (K)	296(2)
Refl. measured	8853
Indep. refl. obs. [$I > 2\sigma(I)$]	5042
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0289$, $wR_2 = 0.0718$
Final *R* indices (all data)	$R_1 = 0.0437$, $wR_2 = 0.0833$
Goodness-of-fit	1.098
Parameters refined	256
Residual density: max., min. (e Å^{-3})	0.358, −0.472

MHz, C_6D_6): $\delta = 41.06$ (s). Anal. Calc. for $C_{22}H_{19}Cl_2PSTi$: C 56.79, H 4.12. Found: C 57.16, H 4.13.

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_2Cl_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_α radiation, $\lambda = 0.7107$ Å). The reflections were corrected for Lp effects using the program MOLEN [21a] and for absorption using ψ-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: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

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