

Thiolate derivatives of bis(diphenylphosphinocyclopentadienyl)titanium Ti–Pt and Ti–Pd heterobimetallic compounds

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Abstract

Reactions of $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{TiCl}_2]$ with HSR in the presence of Et_3N gave the new compounds $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{Ti}(\text{SR})_2]$ ($\text{R} = \text{CH}_2\text{C}_6\text{H}_5$ (1), C_6H_5 (2), CH_2CH_3 (3), C_6F_5 (4) and $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{TiCl}(\text{SC}_6\text{H}_{11})]$ (5). The complex $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{Ti}(\text{SC}_6\text{F}_5)_2]$ can be prepared in higher yield by reaction of TiSC_6F_5 with $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{TiCl}_2]$ in toluene. These compounds are of interest as metalloligands to form bimetallic and trimetallic species. The treatment of $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{TiCl}_2]$ or $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{Ti}(\text{SC}_6\text{H}_5)_2]$ with *cis*- $[\text{M}(\text{C}_6\text{F}_5)_2(\text{THF})_2]$ gave the new heterobimetallic complexes $[\text{Cl}_2\text{Ti}(\mu\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2)_2\text{M}(\text{C}_6\text{F}_5)_2]$ [$\text{M} = \text{Pt}$ (6) or Pd (7)] and $[(\text{C}_6\text{H}_5\text{S})_2\text{Ti}(\mu\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2)_2\text{Pt}(\text{C}_6\text{F}_5)_2]$ (8). In all cases the THF of the *cis*- $[\text{M}(\text{C}_6\text{F}_5)_2(\text{THF})_2]$ was easily replaced by the phosphine rather than chloride or thiolate. The compounds have been characterized by ^1H , ^{31}P and ^{19}F NMR spectroscopies and FAB mass spectrometry.

Keywords: Heterobimetallics; Platinum; Cyclopentadienyl; Palladium; Thiolate; Titanium

1. Introduction

There is a current interest in the synthesis of heterobimetallic compounds that contain both electron-deficient and electron-rich transition metals, as such systems may show enhanced cooperative reactivity [1]. Mononuclear compounds with heterodifunctional ligands containing a cyclopentadienyl ring with a phosphine substituent have received comparatively little attention compared with classical ligands, but recently they have been used to prepare some bimetallic compounds [2].

It is also well known that thiolate ligands form $\text{M}(\mu\text{-SR})\text{M}$ bridges. Stephan *et al.* [3] are developing interesting chemistry in this field.

In connection with our current research projects concerning thiolate derivatives of transition metals, we report here the synthesis and characterization of new thiolate derivatives of formula $[\{\eta^5\text{-C}_5\text{H}_4\text{-P}(\text{C}_6\text{H}_5)_2\}_2\text{-}$

$\text{Ti}(\text{SR})_2]$ ($\text{R} = \text{CH}_2\text{C}_6\text{H}_5$ (1), C_6H_5 (2), CH_2CH_3 (3), or C_6F_5 (4) and $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{TiCl}(\text{SC}_6\text{H}_{11})]$ (5). In order to prepare new heterobimetallic species, we have also studied the ability of the $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{TiCl}_2]$ and $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{Ti}(\text{SC}_6\text{H}_5)_2]$ to coordinate to fragments *cis*- $\text{M}(\text{C}_6\text{F}_5)_2$ ($\text{M} = \text{Pd}$ or Pt) through the phosphine rather than chloride or thiolate.

2. Results and discussion

2.1. $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{TiCl}_2]$

In a short communication Leblanc *et al.* [4] described the synthesis of $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{TiCl}_2]$ by reaction of TiCl_4 and $\text{Li}[\text{C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2]$. In this paper we report a modified method to prepare this titanium metallocene dichloride by reaction of $[\text{TiCl}_4(\text{THF})_2]$ and $\text{Ti}[\text{C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2]$ in toluene. We have compared both methods and found that the latter gives $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{TiCl}_2]$ in a higher yield and purity.

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Table 1
 ^1H , ^{31}P and ^{19}F NMR data (ppm) for complexes 1–8

Complexes	^1H NMR ^a	^{31}P NMR ^b	^{19}F NMR ^c
1	4.29 (s, 4H, CH ₂); 6.04 (m, 4H, C ₅ H ₄); 6.15 (m, 4H, C ₅ H ₄); 7.30 (m, 10H, C ₆ H ₅ ^d); 7.35 (m, 20H, C ₆ H ₅ ^e)	– 14.2 (s)	
2	6.01 (t, 4H, C ₅ H ₄ , <i>J</i> = 2.4 Hz); 6.20 (t, 4H, C ₅ H ₄ , <i>J</i> = 2.4 Hz); 7.29 (m, 10H, C ₆ H ₅ ^f); 7.33 (m, 20H, C ₆ H ₅ ^e)	– 12.6 (s)	
3	1.17 (t, 6H, CH ₃ , <i>J</i> = 7.3 Hz); 3.08 (qu, 4H, CH ₂ , <i>J</i> = 7.3 Hz); 5.88 (m, 4H, C ₅ H ₄); 5.92 (m, 4H, C ₅ H ₄); 7.29 (m, 20H, C ₆ H ₅ ^e)	– 14.7 (s)	
4	6.00 (t, 4H, C ₅ H ₄ , <i>J</i> = 2.5 Hz); 6.16 (t, 4H, C ₅ H ₄ , <i>J</i> = 2.5 Hz) 7.32 (m, 20H, C ₆ H ₅ ^e)	– 12.4 (s)	– 129.8 (d, 1F, <i>o</i> -C ₆ F ₅); – 156.9 (t, 2F, <i>p</i> -C ₆ F ₅); – 162.6 (t, 2F, <i>m</i> -C ₆ F ₅)
5	3.84; 2.04–1.15 (m, 11H, C ₆ H ₁₁); 6.07 (m, 2H, C ₅ H ₄); 6.22 (m, 2H, C ₅ H ₄); 6.25 (m, 2H, C ₅ H ₄); 6.34 (m, 2H, C ₅ H ₄); 7.30 (m, 20H, C ₆ H ₅ ^e)	– 14.2 (s)	
6	6.73 (s, 4H, C ₅ H ₄); 7.11 (s, 4H, C ₅ H ₄); 7.35 (m, 20H, C ₆ H ₅ ^e)	9.96 (s, <i>J</i> _{Pt-P} = 2.339 Hz)	– 117.8 (m, 1F, <i>o</i> -C ₆ F ₅ , <i>J</i> _{Pt-F_o} = 306.5 Hz); – 161.8 (t, 2F, <i>p</i> -C ₆ F ₅); – 163.3 (m, 2F, <i>m</i> -C ₆ F ₅)
7	6.72 (s, 4H, C ₅ H ₄); 7.07 (s, 4H, C ₅ H ₄); 7.40 (m, 20H, C ₆ H ₅ ^e)	14.47 (s)	– 115.7 (m, 1F, <i>o</i> -C ₆ F ₅); – 161.1 (t, 2F, <i>p</i> -C ₆ F ₅); – 162.5 (m, 2F, <i>m</i> -C ₆ F ₅)
8	6.20 (s, 4H, C ₅ H ₄); 6.69 (s, 4H, C ₅ H ₄); 7.60 (m, 20H, C ₆ H ₅ ^e)	9.51 (s, <i>J</i> _{Pt-P} = 23.59 Hz)	– 117.7 (d, 1F, <i>o</i> -C ₆ F ₅ , <i>J</i> _{Pt-F_o} = 306 Hz); – 162.3 (t, 2F, <i>p</i> -C ₆ F ₅); – 163.5 (m, 2F, <i>m</i> -C ₆ F ₅)

^a Relative to trimethylsilane, CDCl₃ solvent. ^b Relative to H₃PO₄, CDCl₃ solvent. ^c Relative to CCl₃F, CDCl₃ solvent. ^d SCH₂C₆H₅.
^e P(C₆H₅)₂. ^f SC₆H₅.

We have also confirmed that reaction time and solvent play an important role in this synthesis.

2.2. $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{Ti}(\text{SR})_2]$ and $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{TiCl}(\text{SC}_6\text{H}_{11})]$

The substitution of chloride by thiolate has been achieved by the reaction of thiol, HSR, with $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{TiCl}_2]$ in toluene in the presence of Et₃N. Different reaction times and stoichiometries were required depending on the thiol. The reaction of TiSC₆F₅ and $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{TiCl}_2]$ gives $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{Ti}(\text{SC}_6\text{F}_5)_2]$ in high yield. The substitution of

the two chlorides of the titanium metallocene dichloride by two cyclohexylthiolates was not possible under the conditions we tried, perhaps due to the steric bulk of this thiolate.

The new complexes were characterised by elemental analyses as well as by IR, ^1H , ^{31}P and ^{19}F NMR spectroscopies (Table 1) and FAB mass spectrometry (Table 2). The ^1H NMR spectra were assigned unambiguously. The two resonances of the cyclopentadienyl rings in the starting material are shifted to higher field in the new compounds. In $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{TiCl}(\text{SC}_6\text{H}_{11})]$ the ^1H NMR spectrum shows four signals, indicating that all protons of the cyclopentadienyl

Table 2
 FAB mass spectra of compounds 1–8 ^a

1	701 (M ⁺ –CH ₂ Ph), 667 (M ⁺ –SCH ₂ Ph), 578 (M ⁺ –SCH ₂ Ph–CH ₂ Ph), 546 (M ⁺ –2SCH ₂ Ph), 250 (C ₅ H ₅ PPh ₂), 201 (O=PPh ₂)
2	764 (M ⁺), 687 (M ⁺ –Ph), 655 (M ⁺ –SPh), 578 (M ⁺ –SPh–Ph), 546 (M ⁺ –2SPh), 250 (C ₅ H ₅ PPh ₂), 201 (O=PPh ₂)
3	668 (M ⁺), 639 (M ⁺ –Et), 607 (M ⁺ –SEt), 578 (M ⁺ –SEt–Et), 546 (M ⁺ –2SEt), 266 (C ₅ H ₅ P(O)Ph ₂), 250 (C ₅ H ₅ PPh ₂), 201 (O=PPh ₂)
4	754 (M ⁺ –SC ₆ F ₅), 578 (M ⁺ –SC ₆ F ₅ –C ₆ F ₅), 546 (M ⁺ –2SC ₆ F ₅), 266 (C ₅ H ₅ P(O)Ph ₂), 250 (C ₅ H ₅ PPh ₂), 201 (O=PPh ₂)
6	1111 (M ⁺ –Cl), 979 (M ⁺ –C ₆ F ₅), 942 (M ⁺ –C ₆ F ₅ –Cl), 862 (M ⁺ –C ₅ H ₄ PPh ₂ –Cl), 811 (M ⁺ –2C ₆ F ₅), 777 (M ⁺ –2C ₆ F ₅ –Cl), 742 (M ⁺ –2C ₆ F ₅ –2Cl), 695 [(C ₅ H ₄ PPh ₂)TiCl(C ₆ F ₅)P]
7	724 (M ⁺ –2C ₆ F ₅), 687 (M ⁺ –2C ₆ F ₅ –Cl), 652 (M ⁺ –2C ₆ F ₅ –2Cl), 475 [Pd(PPh ₂) ₂], 417 [(C ₅ H ₄ PPh ₂)(C ₆ F ₅)]
8	1185 (M ⁺ –SPh), 1075 (M ⁺ –2SPh), 741 (M ⁺ –2C ₆ F ₅ –2SPh), 359 [(C ₅ H ₄ PPh ₂)(SPh)]

^a Matrix: 3-nitrobenzylalcohol (NBA).

ring are magnetically inequivalent. The spectra show also the resonances expected for the different thiolates.

The ^{31}P NMR spectra of CDCl_3 solutions at room temperature show one signal of about -13.5 ppm, indicating the equivalence of both phosphorus atoms of the PPh_2 substituent of the cyclopentadienyl ring.

The ^{19}F NMR spectrum of $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{Ti}(\text{SC}_6\text{F}_5)_2]$ is similar to those reported for other perfluorophenylthiolate derivatives [5]. The *ortho*- and *meta*-fluorine signals appear as a doublet and a triplet at -129.8 and -162.6 ppm, respectively, and the *para*-fluorine signal as a triplet at -156.9 ppm.

The positive-ion FAB mass spectra were recorded using 3-nitrobenzylalcohol as the matrix and THF as solvent. A weak signal corresponding to the molecular ion appeared only in the phenyl- and ethyl-thiolate derivatives. A similar fragmentation pattern is observed for all the compounds. The peaks observed in the spectra are consistent with the presence of the different thiolate and cyclopentadienyl ligands.

2.3. $[\text{Cl}_2\text{Ti}\{\mu\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{M}(\text{C}_6\text{F}_5)_2]$ ($\text{M} = \text{Pt}$ or Pd) and $[(\text{C}_6\text{H}_5\text{S})_2\text{Ti}\{\mu\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{Pt}(\text{C}_6\text{F}_5)_2]$

Mononuclear compounds with (phosphino)cyclopentadienyl ligands are useful for preparing homo- or hetero-bimetallic complexes. Literature reports on the use of dichloro bis[(diphenylphosphino)cyclopentadienyl]titanium as a ligand are scarce. As far as we know, only Schenk and Newland-Labude [6] have described the preparation of some Ti-M ($\text{M} = \text{Cr}, \text{Mo}$ or W) heterobimetallic compounds using that reagent. On the other hand Stephan *et al.* [3], among others, have reported the use of thiolate derivatives of titanium metallocene reagents to synthesise bimetallic compounds. In order to expand this field, we studied the competition between the phosphine and chloride in $[\{\eta^5\text{-C}_5\text{H}_4(\text{C}_6\text{H}_5)_2\}_2\text{TiCl}_2]$ and phosphine and thiolate in $[\{\eta^5\text{-C}_5\text{H}_4(\text{C}_6\text{H}_5)_2\}_2\text{Ti}(\text{SC}_6\text{H}_5)_2]$ in reaction with *cis*- $[\text{M}(\text{C}_6\text{F}_5)_2(\text{THF})_2]$ ($\text{M} = \text{Pt}$ or Pd). By addition of *cis*- $[\text{M}(\text{C}_6\text{F}_5)_2(\text{THF})_2]$ ($\text{M} = \text{Pt}$ or Pd) to a suspension of $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{TiCl}_2]$ in toluene, $[\text{Cl}_2\text{Ti}\{\mu\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{M}(\text{C}_6\text{F}_5)_2]$ were obtained. These compounds are quite unstable in solution. In both cases the THF has been replaced by phosphine instead of chloride, giving new heterobimetallic complexes $[\text{Cl}_2\text{Ti}\{\mu\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{M}(\text{C}_6\text{F}_5)_2]$ [$\text{M} = \text{Pt}$ (6), Pd (7)]

The spectroscopic data of the Pt-Ti and Pd-Ti compounds are similar. These are collected in Table 1. The ^1H NMR spectrum consists of two singlets shifted to a lower field than those observed for the mononuclear titanium derivatives, and corresponding to the cyclopentadienyl rings, and also a multiplet for the phenyl groups.

In the ^{31}P NMR spectrum a single resonance with a Pt-P coupling constant is observed, in the range found

for other (diphenylphosphinocyclopentadienyl)platinum compounds [7]. The shift of the P signal to higher field is indicative of coordination through phosphorus.

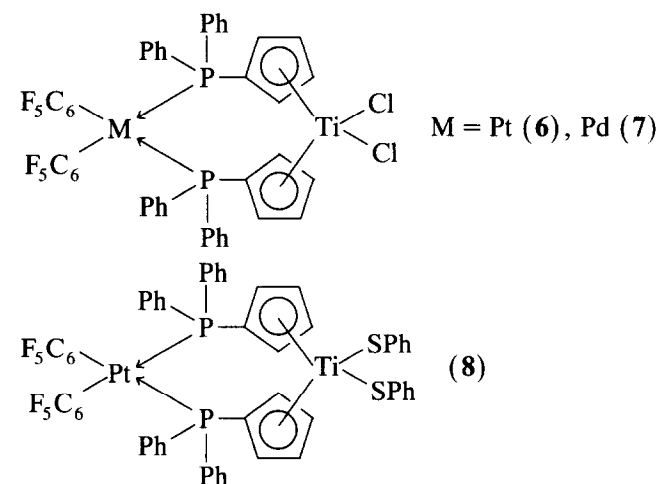
The ^{19}F NMR spectra of $[\text{Cl}_2\text{Ti}\{\mu\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{M}(\text{C}_6\text{F}_5)_2]$ display the characteristic pattern for this type of compound. Pt-F coupling is observed in the Pt-Ti compounds.

No molecular peaks are observed in the mass spectra, but there are fragmentation peaks indicating the loss of various ligands. (Table 2).

When a toluene solution of *cis*- $[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{THF})_2]$ was treated with one equivalent of $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{Ti}(\text{SC}_6\text{H}_5)_2]$ the compound $[(\text{C}_6\text{H}_5\text{S})_2\text{Ti}\{\mu\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{Pt}(\text{C}_6\text{F}_5)_2]$ was isolated. ^1H , ^{31}P and ^{19}F NMR spectra (Table 1) show resonances comparable to those found for $[\text{Cl}_2\text{Ti}\{\mu\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{Pt}(\text{C}_6\text{F}_5)_2]$ (6), indicating a similar structure. The compound show a similar pattern in the mass spectrum (Table 2). The reaction of *cis*- $[\text{Pd}(\text{C}_6\text{F}_5)_2(\text{THF})_2]$ and $[\{\eta^5\text{-C}_5\text{H}_4(\text{C}_6\text{H}_5)_2\}_2\text{Ti}(\text{SC}_6\text{H}_5)_2]$ gave a mixture of unidentified products. The structures of compounds 6, 7 and 8 are given in Scheme 1.

3. Experimental details

All reactions were carried out under a nitrogen atmosphere using Schlenk techniques. Solvents were dried by standard methods [8]. The starting materials $\text{Ti}[\text{C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2]$ [9], $[\text{TiCl}_4(\text{THF})_2]$ [10], and *cis*- $[\text{M}(\text{C}_6\text{F}_5)_2(\text{THF})_2]$ ($\text{M} = \text{Pd}$ or Pt) [11] were prepared as described previously, and all other reagents were commercially available. Elemental analyses for C and H were performed with Perkin Elmer 2400 and Perkin Elmer 240-B microanalysers. IR spectra were recorded on a Perkin Elmer 1600 FT-IR spectrophotometer. NMR spectra were recorded on a Bruker AMX-300 (^1H) Varian Unity 300 and Bruker ARX-300 (^{19}F) and Bruker AC 300 (^{31}P) instruments. FAB positive ion mass spectra were measured on a VG Autospec spectrometer.



Scheme 1.

3.1. Synthesis of $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{TiCl}_2]$

This is a modified synthesis of a previous procedure [4]. The compound $[\text{TiCl}_4(\text{THF})_2]$ (2.45 g, 7.06 mmol) was added to a suspension of $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2]$ (6.40 g, 14.12 mmol) in toluene (35 cm³). After 4 h stirring at room temperature, the resultant red–brown solution was filtered through a pad of Celite and the solvent was removed *in vacuo*. The residue was washed with (4 × 10 cm³) portions of cold diethyl ether, leaving the product as a light red–brown solid in *ca.* 65% yield.

¹H-NMR (CDCl₃): 6.48 (m, 4H, C₅H₄); 6.52 (m, 4H, C₅H₄); 7.32 (m, 20H, C₆H₅). ³¹P-NMR (CDCl₃): –11.0 (s).

3.2. Synthesis of $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{Ti}(\text{SCH}_2\text{C}_6\text{H}_5)_2]$ (1)

To a solution of $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{TiCl}_2]$ (0.28 g, 0.45 mmol) in toluene (30 cm³), HSCH₂C₆H₅ (0.24 cm³, 2.0 mmol) and Et₃N (0.36 cm³, 2.15 mmol) were added. After stirring at room temperature for 15 h, the solution was filtered through silica gel and by removing the solvent, a deep violet solid was isolated. Recrystallisation from toluene–hexane (1:1) at –20 °C gave violet crystals (0.27 g, 76% yield). Found: C, 73.16; H, 5.50; Calc. for C₄₈H₉₂P₂S₂Ti: C, 72.72; H, 5.34%.

3.3. Preparation of $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{Ti}(\text{SC}_6\text{H}_5)_2]$ (2)

This compound was obtained following the above procedure but with 1:2 stoichiometry (60% yield). Found: C, 73.10; H, 5.01; Calc. for C₄₆H₃₈P₂S₂Ti: C, 72.24; H, 5.2%.

3.4. Preparation of $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{Ti}(\text{SCH}_2\text{-CH}_3)_2]$ (3)

This compound was prepared following the above procedure but with 1:2 stoichiometry and 40 h reaction time. The solution was then filtered through a pad of Celite and, by removing the solvent, an oily compound was obtained which was washed with hexane (3 × 10 cm³) at –60 °C giving a violet solid. Recrystallisation from toluene–hexane (1:1) gave the pure compound (80% yield). Found: C, 68.06; H, 5.35; Calc. for C₃₈H₃₈P₂S₂Ti: C, 68.25; H, 5.73%.

3.5. Preparation of $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{Ti}(\text{SC}_6\text{F}_5)_2]$ (4)

To a toluene solution (20 cm³) of $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{TiCl}_2]$ (0.12 g; 0.2 mmol) was added TlSC₆F₅ (0.16 g; 0.4 mmol). After stirring for 3.5 h at room temperature the solution was filtered through a pad of

Celite and the solvent was removed *in vacuo*. The resulting residue was crystallised from toluene–hexane (1:1) at –20 °C. (72% yield). Found: C, 57.09; H, 3.23; Calc. for C₄₆H₂₈F₁₀P₂S₂Ti: C, 58.49; H, 2.99%.

3.6. Preparation of $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{TiCl}(\text{SC}_6\text{H}_{11})]$ (5)

This compound was prepared following the method indicated for (3) from using 1:2 stoichiometry and 15 h reaction time (82% yield). Found: C, 65.09; H, 5.60; Calc. for C₄₀H₃₉ClP₂STi: C, 66.32; H, 5.60%.

3.7. Preparation of $[\text{Cl}_2\text{Ti}\{\mu\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{Pt}(\text{C}_6\text{F}_5)_2]$ (6)

Cis-[Pt(C₆F₅)₂(THF)₂] (0.164 g, 0.243 mmol) was added to a stirred red–brown suspension of $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{TiCl}_2]$ (0.150 g, 0.243 mmol) in toluene (20 cm³). The mixture was stirred at room temperature for 5 min and then filtered through a plug of Celite and silica gel 1:1 on a frit. The resulting orange–red solution was evaporated to dryness and hexane was added to the residue, affording an orange–rose solid (6) which was filtered off and washed with hexane (0.084 g, 30% yield). Found: C, 48.48; H, 3.07; Calc. for C₄₆H₂₈Cl₂F₁₀P₂PtTi: C, 48.19; H, 2.46%.

3.8. Preparation of $[\text{Cl}_2\text{Ti}\{\mu\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{Pd}(\text{C}_6\text{F}_5)_2]$ (7)

The synthesis was performed as described for complex 6 starting from $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{TiCl}_2]$ and *cis*-[Pd(C₆F₅)₂(THF)₂] (37% yield). Found: C, 51.43; H, 3.11. Calc. for C₄₆H₂₈Cl₂F₁₀P₂PdTi: C, 52.23; H, 2.67%.

3.9. Preparation of $[(\text{C}_6\text{H}_5\text{S})_2\text{Ti}\{\mu\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{Pt}(\text{C}_6\text{F}_5)_2]$ (8)

To a dark solution of $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{Ti}(\text{SC}_6\text{H}_5)_2]$ (0.150 g, 0.196 mmol) in toluene (30 cm³) was added *cis*-[Pt(C₆F₅)₂(THF)₂] (0.132 g, 0.196 mmol) and the mixture was stirred at room temperature for 2 h. The resulting turbid solution was evaporated to *ca.* 10 cm³ and filtered. The solvent was removed from the dark green filtrate and hexane was added to the residue affording a deep green solid which was filtered off and washed with hexane. (0.13 g, 51% yield). Found: C, 53.45; H, 3.35; S, 4.63. Calc. for C₅₈H₃₈F₁₀P₂PtS₂Ti: C, 53.84; H, 2.96; S, 4.95%.

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