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Mono(cyclopentadienyl)titanium complexes containing a sulfide-bridged bis(phenolato) ligand. Molecular structure of Ti{2,2′-S(OC_6H_2-4-Me-6-^{t}Bu)$_2$}(η^5-C_5H_5)Cl

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Dedicated to Professor H. Brunner on the occasion of his 65th birthday

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Abstract

A series of titanium complexes containing a sulfur-bridged chelating bis(phenolato) ligand, Ti{2,2′-S(OC_6H_2-4-Me-6-^{t}Bu)$_2$}(η^5-C_5R_5)Cl (R = H, Me; R_5 = 1,3-$(SiMe_3)_2H_3$), were prepared by the reaction of the dilithium derivative Li_2[2,2′-S(OC_6H_2-4-Me-6-^{t}Bu)$_2$] with Ti(η^5-C_5R_5)Cl_3. Alkylation of the chloro complexes gave complexes of the type Ti{2,2′-S(OC_6H_2-4-Me-6-^{t}Bu)$_2$}-(η^5-C_5R_5)R′ (R′ = Me, CH_2Ph). The crystal structure of the chloro complex Ti{2,2′-S(OC_6H_2-4-Me-6-^{t}Bu)$_2$}(η^5-C_5H_5)Cl has been determined by X-ray diffraction and shows a monomeric four-legged piano-stool structure with the sulfur and chlorine atoms in *trans* positions. A long titanium–sulfur bond length of 2.907(1) Å was observed.

Keywords: Titanium complexes; Sulfur donor; Cyclopentadienyl ligand; Phenolato ligand

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1. Introduction

Titanium(IV) half-sandwich complexes of the type Ti(η^5-C_5R_5)X_3 (X = one-electron ligand) can in principle accommodate up to three two-electron ligands L [1]. The full 18-electron configuration is not very frequently encountered, since various degrees of π-donation may occur to attenuate the Lewis-acidity [2]. Alkoxo and phenoxo ligands are particularly variable monoanionic ligands in this respect and have found application as controlling ligands in several instances [3]. We have been interested in the use of linked bis(phenolato) ligands of the general type 2,2′-*Z*(OC_6H_2-4-Me-6-^{t}Bu) where the link *Z* between the two bulky phenolato moieties is varied systematically [4]. In particular, the sulfide bridged system tbmp (*Z* = S) is important as ancillary ligand in olefin polymerization catalysis [5]. We report here the synthesis of several alkyl derivatives of the Ti(tbmp) fragment.

2. Results and discussion

As reported earlier [4b], the reaction between cyclopentadienyl lithium and the dichloro titanium complex with a sulfide-linked bis(phenolato) ligand, $[Ti(tbmp)Cl_2]_2$ (tbmp = 2,2′-thiobis(6-*tert*-butyl-4-methylphenolato)), gives mono(cyclopentadienyl)titanium complexes Ti(tbmp)(η^5-C_5R_5)Cl (R = H, **1**; R = Me, **4**), as shown in Eq. (1).

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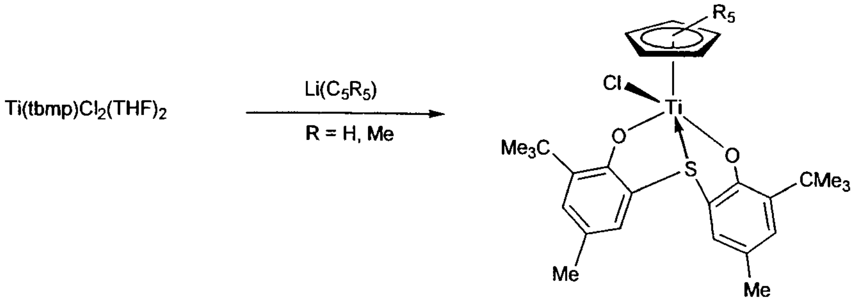
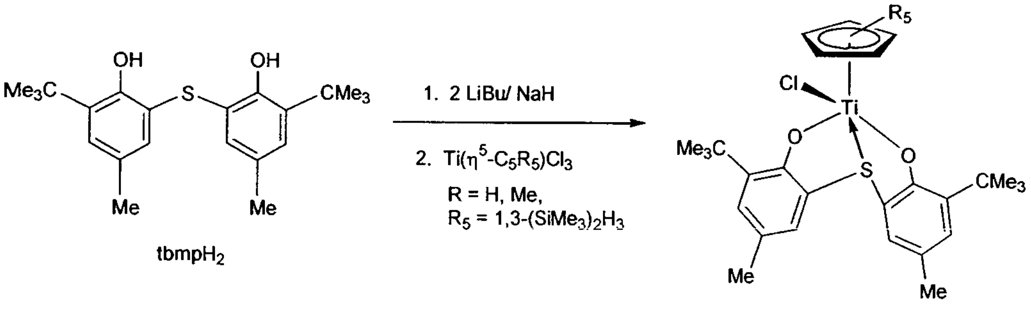


R = H, **1**
R = Me, **4** (1)

These complexes, together with the new derivative Ti(tbmp){η^5-1,3-$(SiMe_3)_2C_5H_3$}Cl (**6**), are also accessible from the metathesis reaction between the appropriate trichloro titanium derivatives Ti(η^5-C_5R_5)Cl_3 (R = H, Me; R_5 = 1,3-$(SiMe_3)_2H_3$) and the dilithium or disodium salts of the tbmp ligand in approximately the same yields as via the previously reported method (Eq. (2)). These reactions can be carried out in separate steps or as a one-pot reaction with no significant differences in the yields. The chloro derivatives are obtained as red crystals which are soluble in ethers and slightly soluble in aliphatic hydrocarbons.



R = H, **1**
R = Me, **4**
R_5 = 1,3-$(SiMe_3)_2H_3$, **6** (2)

The ^{1}H-NMR spectra of the complexes **1**, **4** and **6** show one singlet for all the equivalent methyl groups of the *tert*-butyl substituents on the phenyl rings and one singlet for the two methyl substituents on the phenyl rings, while the protons of the phenyl ring at position 3 and 5 appear as two doublets ($^4J_{HH}$ ca. 2 Hz). The signals for the protons, methyl and trimethylsilyl substituents on the cyclopentadienyl rings are observed in the expected region. Based on similar mass spectral as well as ^{1}H- and ^{13}C-NMR spectroscopic data of **4** and **6** to those of the parent complex **1**, a structure analogous to that of crystallographically characterized **1** can be implied for both compounds[1]. Crystals of **1** suitable for single-crystal X-ray diffraction were obtained by slow crystallization from a diethyl ether/hexane mixture. Fig. 1 shows an ORTEP plot of the molecular structure of **1** and Table 1 summarizes selected bond distances and angles.

Complex **1** crystallized with diethyl ether in the unit cell. The coordination sphere around the titanium center in **1** can be described as that of a four-legged piano-stool in which the chlorine atom is located in *trans*-position to the sulfur atom. The angles O–Ti–S and O–Ti–Cl range from 70.42(5) to 95.08(6)° with a sum of 328.51°. The titanium–sulfur bond length of 2.907(1) Å is one of the largest so far reported in the literature [4b,6], although it is still smaller than the sum of the van der Waals radii of the two atoms [7]. This may suggest a weaker interaction between the sulfur atom and the metal center than those reported for other titanium–thioether complexes adducts as Ti(η^5-C_5H_5)($SCH_2CH_2SCH_2CH_2S$) (2.600(1) Å) [8a], $TiCl_4(HSC_6H_{11})_2$ (av. 2.664 Å) [8b], [Ti(η^5-C_5H_5)(SCH_2CH_2S)Cl]$_2$ (av. 2.513 Å) [8c], Ti(N^{t}Bu)Cl_2(9-aneS_3) (av. 2.638 Å) [8d] and *cis*-$TiCl_4(S(CH_2)_4)_2$ (av. 2.265 Å) [8e]. The tbmp ligand

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[1] The X-ray diffraction study on a single crystal of **6** shows a structure similar to that of **1** with a position for the chlorine atom *trans* to the sulfur atom. Red crystal, 0.13 × 0.53 × 0.63 mm^3, a = 9.484(2), b = 20.623(6), c = 18.680(3) Å, $\alpha = \gamma = 90°$, $\beta = 99.86(2)°$, V = 3600(1) Å^3, tentative space group $P2_1/c$. The poor quality of the crystallographic data preclude further discussion of the results.

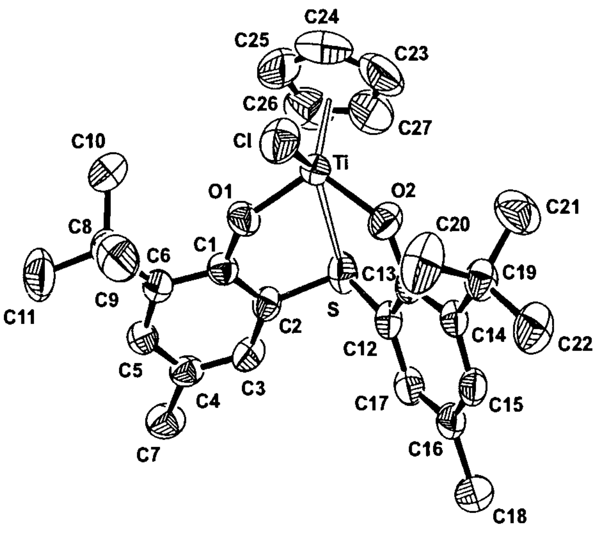


Fig. 1. ORTEP diagram of the molecular structure of Ti(tbmp)(η^5-C_5H_5)Cl (**1**). Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for the sake of clarity. The Et_2O solvent molecule is also excluded.

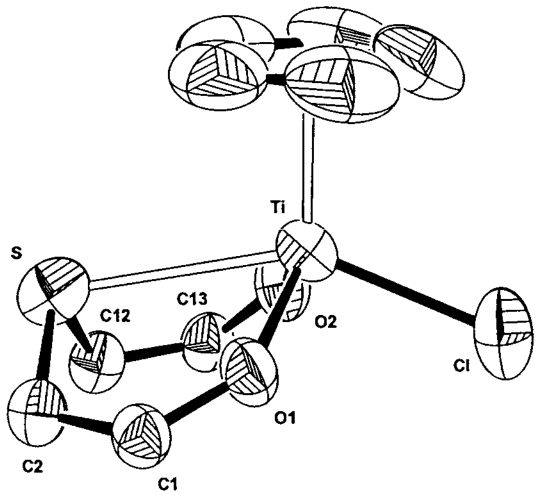


Fig. 2. View of the eight-membered ring conformation in Ti(tbmp)(η^5-C_5H_5)Cl (**1**).

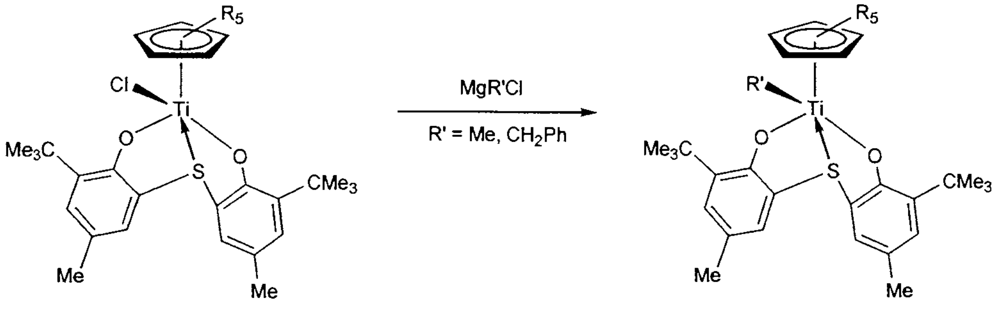
Table 1
Selected bond lengths (Å) and bond angles (°) for Ti(tbmp)(η^5–C_5H_5)Cl (**1**)

Bond lengths		*Bond angles*	
Ti–Cl	2.318(1)	Cl–Ti–O(1)	92.50(6)
Ti–S	2.907(1)	Cl–Ti–O(2)	95.08(6)
Ti–O(1)	1.827(2)	S–Ti–O(1)	70.42(5)
Ti–O(2)	1.827(2)	S–Ti–O(2)	70.51(6)
Ti–C(23)	2.379(3)	S–Ti–Cl	148.23(3)
Ti–C(24)	2.380(3)	O(1)–Ti–O(2)	115.59(8)
Ti–C(25)	2.373(3)	Ti–O(1)–C(1)	141.9(1)
Ti–C(26)	2.349(3)	Ti–O(2)–C(13)	137.8(1)
Ti–C(27)	2.354(4)	C(2)–S–C(12)	107.3 (1)
S–C(2)	1.769(2)	Ti–S–C(2)	91.93(7)
S–C(12)	1.773(2)	Ti–S–C(12)	89.93(8)
O(1)–C(1)	1.344(2)		
O(2)–C(13)	1.349(3)		

adopts the typical boat conformation observed in other complexes [4b,6] with the sulfur atom pointing towards the metal center in the proximity of the cyclopentadienyl ring (see Fig. 2). This is probably due to the electron donating effect of the cyclopentadienyl ligand and the steric hindrance of the *tert*-butyl groups. A similar configuration is adopted by other related linked bis(phenolato) ligands with a sulfinyl [4d], oxo [9], tellurium [10] and methylene bridge [11]. The metal–oxygen bond lengths of 1.827(2) Å are in the expected range for titanium complexes with a linked bis(phenolato) ligand (av. 1.892 Å in [Ti{2,2′-S(OC_6H_2-4-Me-6-^{t}Bu$)_2$}(O^{i}Pr$)_2$$]_2$ and av. 1.855 Å in Ti{2,2′-S(OC_6H_2-4-Me-6-^{t}Bu$)_2$}(*o*-$CH_2NMe_2C_6H_4$)Cl [4b], av. 1.888 Å in Ti{2,2′-S(OC_6H_2-4-Me-6-^{t}Bu$)_2$}Br_2 [6], av. 1.872 Å in Ti{2,2′-Te(OC_6H_2-4-Me-6-^{t}Bu$)_2$}(η^5-C_5Me_5)Cl [10], av. 1.751 Å in Ti{2,2′-CH_2(OC_6H_2-4-Me-6-^{t}Bu$)_2$}Cl_2 [11a], av. 1.776 Å in Ti{2,2′-CH_2(OC_6H_2-4-Me-6-^{t}Bu$)_2$}$(BH_4)_2$ [11b], av. 1.788 Å in Ti{2,2′-CH_2(OC_6H_2-4-Me-6-^{t}Bu$)_2$}(*o*-$CH_2NMe_2C_6H_4$)(OSO_2CF_3) [11d], and av. 1.81 Å in Ti{2,2′-(OC_6H_2-4-OMe-6-^{t}Bu$)_2$}$(CH_2Ph)_2$ [12]). Values larger than those found for titanium complexes with a non-linked alkoxo ligand as Ti(OC_6H_3-2,6-^{t}Bu$_2$)$Cl_3(THF)_2$ (1.807(8) Å) [9], Ti$(OPh)_2Cl_2$ (1.744(10) Å) [13a], Ti(OC_6H_3-2,6-$Ph_2$$)_2Cl_2$ (1.726(2) Å) [13b], [Ti(OC_6H_3-2,6-$Ph_2$$)_2]_2$($\eta$-Cl$)_2$ (av. 1.817 Å) [13c], Ti(OC_6H_3-2,6-$Me_2$$)_2Cl_2(THF)_2$ (av. 1.788 Å) [13d], and Ti(OC_6H_3-2,6-^{i}Pr$_2$)(η^5-C_5H_5)(SPh)Cl (1.80(2) Å) [13e] may suggest a decrease in the π-donation from the oxygen atoms to the metal center [14].

Metathesis reactions of the chloro complexes **1**, **4** and **6** with alkylating reagents MgMeCl or Mg(CH_2Ph)Cl resulted in the formation of alkyl complexes Ti(tbmp)(η^5-C_5R_5)R′ (R = H, R′ = Me (**2**), CH_2Ph (**3**); R = Me, R′ = Me (**5**); R_5 = 1,3-$(SiMe_3)_2H_3$, R′ = Me (**7**), CH_2Ph (**8**)) in moderate yields (68–75%) (Eq. (3)). The complexes **2** and **5** are orange, the complexes **3** and **7** are dark yellow and the complex **8** is brown. They are all soluble in aliphatic hydrocarbons. The reaction of the chloro complex **4** with Mg(CH_2Ph)Cl in THF at − 78°C results in the formation of a yellow reaction mixture, but upon work-up the starting material was recovered.

For the methyl complexes **2** and **7**, the methyl group at the titanium center are observed as singlets at 1.34 and 1.31 ppm, respectively, in the ^{1}H-NMR spectra, while for complex **5** the corresponding signal is high-field shifted to 0.38 ppm. The ^{13}C-NMR spectroscopic $TiCH_3$ resonances are observed at 58.1 for **2**, 60.8 for **5**, and 60.5 ppm for **7**. The benzyl derivatives **3** and **8** show only one resonance for the two equivalent methylene protons of the benzyl groups at 3.15 ppm and three broad signals for the protons of the benzylic phenyl ring. The ^{1}H-NMR spectra of the alkyl complexes **2**, **3**, **5**, **7** and **8** show patterns for the tbmp ligand similar to those described for the ^{1}H-NMR spectra of the chloro precursors **1**, **4** and **6**: The methyl groups of the *tert*-butyl substituents on the phenolato groups remain equivalent and appear in the region from 1.26 to 1.41 ppm while the methyl substituents on the phenyl rings appear as a singlet at 2.2 ppm. The proton atoms on the phenyl ring are recorded as doublets with a similar coupling constant as in the chloro precursors.



R = H, **1**
R = Me, **4**
R_5 = 1,3-$(SiMe_3)_2H_3$, **6**

R = H, R' = Me, **2**
R = H, R' = CH_2Ph, **3**
R = Me, R' = Me, **5**
R_5 = 1,3-$(SiMe_3)_2H_3$, R' = Me, **7**
R_5 = 1,3-$(SiMe_3)_2H_3$, R' = CH_2Ph, **8**

(3)

This work shows that the Ti(tbmp) fragment is stabilized by a cyclopentadienyl ligand and alkylation of the remaining chloro function becomes feasible. Previously, we had encountered considerable difficulties in synthesizing the ten-electron dialkyls of the type $Ti(tbmp)R_2$ by alkylating the dichloro complex $Ti(tbmp)Cl_2$ Such problems do not appear in the preparation of the more stable derivatives Ti(tbmp)(η^5-C_5R_5)R′ which formally have a 14-valence electron configuration.

3. Experimental

All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. Diethyl ether was distilled from sodium benzophenone ketyl. Pentane and hexane were purified by distillation over sodium–benzophenone ketyl–triglyme. $tbmpH_2$ [15], Ti(η^5-C_5H_5)Cl_3 [16], Ti(η^5-C_5Me_5)Cl_3 [17] and Ti{η^5-1,3-$(SiMe_3)_2C_5H_3$}Cl_3 [18] were synthesized according to published procedures. Li^nBu (Aldrich), NaH (Aldrich), MgMeCl (Aldrich) and $Mg(CH_2C_6H_5)Cl$ (Aldrich) were used as received. Lithium [19] and Grignard [20] solutions were titrated prior to use. NMR spectra were recorded on a Bruker DRX 400 or on a Varian Unity 300 spectrometer (^{1}H, 400.1 MHz, 299.9 MHz; ^{13}C, 75.43, 100.6 MHz) in $CDCl_3$ at 298 K. Chemical shifts (in ppm) for ^{1}H and ^{13}C were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane. Mass spectra were recorded on a Finnigan 8230 spectrometer. Elemental analyses were performed by the microanalytical laboratory of this department.

3.1. *Ti(tbmp)(η^5-C_5H_5)Cl (**1**)*

A solution of Li^nBu (2.1 ml of a 1.5 M solution in THF) was added to a solution of $tbmpH_2$ (1.1 g, 3.0 mmol) in hexane (ca. 25 ml) at 0°C and the mixture was stirred for 16 h. The solvents were filtered off and the white precipitate was washed with hexane (2 × 10 ml) and dried in vacuo. A solution of Ti(η^5-C_5H_5)Cl_3 (0.50 g, 2.28 mmol) in diethyl ether (20 ml) was added to a suspension of Li_2(tbmp) (0.90 g, 2.4 mmol) in diethyl ether (15 ml) at −78°C. The mixture was slowly warmed up to room temperature (r.t.) and stirred for 16 h. Concentration of the solution followed by addition of hexane (ca. 20 ml) and cooling to −30°C afford 0.92 g of dark red crystals (80%): ^{1}H-NMR δ 1.25 (s, 18H, 6-$C(CH_3)_3$), 2.21 (s, 6H, 4-CH_3), 6.76 (s, 5H, C_5H_5), 6.98 (d, $^4J_{HH} = 1.6$ Hz, 2H, 5-H), 7.27 (d, $^4J_{HH} = 1.6$ Hz, 2H, 3-H); ^{13}C{^{1}H}-NMR δ 20.8 (4-CH_3), 29.8 (6-$C(CH_3)_3$), 35.2 (6-$C(CH_3)_3$), 119.4 (C_5H_5), 128.3 (C-2), 129.9 (C-5), 130.4 (C-4), 131.6 (C-3), 138.4 (C-6), 167.1 (C-1); EI MS *m*/*z* 504 (86, [M^+]), 439 (100, [$M^+ - C_5H_5$]); Anal. Calc. for $C_{27}H_{33}ClO_2STi$: C, 64.22; H, 6.59. Found: C, 64.35; H, 6.49.

3.2. *Ti(tbmp)(η^5-C_5H_5)Me (**2**)*

Methylmagnesium chloride (0.23 ml of a 3 M solution in THF) was added to a precooled ethereal solution of **1** (0.33 g, 0.66 mmol) at −78°C (ca. 10 ml) and the reaction mixture was allowed to warm slowly to r.t. overnight. All volatiles were removed in vacuo and the residue was extracted with pentane (ca. 30 ml) and the extracts concentrated. Cooling the solution to −78°C overnight precipitated 0.22 g of an orange solid (68%): ^{1}H-NMR δ 1.32 (s, 18H, 6-C(CH$_3$)$_3$), 1.34 (s, TiCH$_3$), 2.29 (s, 6H, 4-CH$_3$), 6.56 (s, 5H, C$_5$H$_5$), 7.06 (d, $^{4}J_{HH}$ = 2 Hz, 2H, 5-H), 7.44 (d, $^{4}J_{HH}$ = 2 Hz, 2H, 3-H); ^{13}C{^{1}H}-NMR δ 20.7 (4-CH$_3$), 29.7 (6-C(*C*H$_3$)$_3$), 35.1 (6-*C*(CH$_3$)$_3$), 58.1 (TiCH$_3$), 115.4 (C$_5$H$_5$), 128.4 (C-2), 128.9 (C-4), 129.4 (C-5), 132.9 (C-3), 137.6 (C-6), 166.1 (C-1); EI MS *m*/*z* 469 (100, M^{+}-CH$_3$); Anal. Calc. for C$_{28}$H$_{36}$O$_2$STi: C, 69.41; H, 7.49. Found: C, 69.34; H, 7.72.

3.3. Ti(tbmp)(η^{5}-C$_5$H$_5$)(CH$_2$Ph) (3)

A solution of **1** (0.40 g, 0.79 mmol) in diethyl ether (ca. 15 ml) was treated with benzylmagnesium chloride (0.77 ml of a 1.24 M solution in THF) at −78°C. After stirring for 16 h at r.t., all volatiles were removed in vacuo. The residue was extracted into hexane (ca. 30 ml) and the solvent was removed. Recrystallization from pentane at −30°C afforded dark yellow crystals (0.30 g, 68%): ^{1}H-NMR δ 1.41 (s, 18H, 6-C(CH$_3$)$_3$), 2.26 (s, 6H, 4-CH$_3$), 3.14 (s, 2H, TiCH$_2$), 6.31 (s, 5H, C$_5$H$_5$), 7.06 (d, $^{4}J_{HH}$ = 2 Hz, 2H, 5-H), 7.26, 7.28, 7.30 (br, 5H, C$_6$*H*$_5$), 7.40 (d, $^{4}J_{HH}$ = 2 Hz, 2H, 3-H); ^{13}C{^{1}H}-NMR δ 20.7 (4-CH$_3$), 29.9 (6-C(*C*H$_3$)$_3$), 35.4 (6-*C*(CH$_3$)$_3$), 81.2 (TiCH$_2$), 117.9 (C$_5$H$_5$), 122.6, 126.4 (C$_6$H$_5$), 128.0 (C-5), 128.9 (C-2), 129.2 (C-4), 129.6 (C$_6$H$_5$), 133.2 (C-3), 137.9 (C-6), 152.4 (*ipso* C$_6$H$_5$), 166.7 (C-1); Anal. Calc. for C$_{34}$H$_{40}$O$_2$STi: C, 72.87; H, 7.14. Found: C, 72.96; H, 7.18.

3.4. Ti(tbmp)(η^{5}-C$_5$Me$_5$)Cl (4)

This compound was prepared following a procedure analogous to that described to prepare **1** from Li$_2$(tbmp) (0.50 g, 1.35 mmol) and Ti(η^{5}-C$_5$Me$_5$)Cl$_3$ (0.37 g, 1.30 mmol) and isolated as red crystals; yield 0.58 g (79%): ^{1}H-NMR δ 1.35 (s, 18H, 6-C(CH$_3$)$_3$), 2.25 (s, 15H, C$_5$(CH$_3$)$_5$), 2.26 (s, 6H, 4-CH$_3$), 7.05 (d, $^{4}J_{HH}$ = 2 Hz, 2H, 5-H), 7.23 (d, $^{4}J_{HH}$ = 2 Hz, 2H, 3-H); ^{13}C{^{1}H}-NMR δ 13.0 (C$_5$(*C*H$_3$)$_5$), 20.9 (4-CH$_3$), 31.8 (6-C(*C*H$_3$)$_3$), 34.8 (6-*C*(CH$_3$)$_3$), 126.5 (C-5), 128.0 (C-3), 129.5 (*C*$_5$(CH$_3$)$_5$), 130.1 (C-4), 131.9 (C-2), 137.7 (C-6), 161.0 (C-1); EI MS *m*/*z* 574 (89, [M^{+}]), 539 (41, [M^{+} − Cl]), 439 (100, [M^{+} − C$_5$Me$_5$]); Anal. Calc. for C$_{32}$H$_{43}$ClO$_2$STi: C, 66.83; H, 7.54. Found: C, 67.05; H, 7.64.

3.5. Ti(tbmp)(η^{5}-C$_5$Me$_5$)Me (5)

Following a procedure analogous to that described to prepare **2**, the chloro complex **4** (0.21 g, 0.36 mmol) was reacted with methylmagnesium chloride (0.13 ml of a 3 M solution in THF) to give orange crystals; yield 0.15 g (75%): ^{1}H-NMR δ 0.86 (s, 3H, TiCH$_3$), 1.27 (s, 18H, 6-C(CH$_3$)$_3$), 2.07 (s, 15H, C$_5$(CH$_3$)$_5$), 2.24 (s, 6H, 4-CH$_3$), 7.01 (d, $^{4}J_{HH}$ = 2 Hz, 2H, 5-H), 7.34 (d, $^{4}J_{HH}$ = 2 Hz, 2H, 3-H); ^{13}C{^{1}H}-NMR δ 12.5 (C$_5$(*C*H$_3$)$_5$), 20.7 (4-CH$_3$), 30.0 (6-C(*C*H$_3$)$_3$), 34.7 (6-*C*(CH$_3$)$_3$), 60.8 (TiCH$_3$), 124.7 (*C*$_5$(CH$_3$)$_5$), 125.3 (C-5), 127.9 (C-2), 129.7 (C-4), 131.9 (C-3), 137.7 (C-6), 165.5 (C-1); EI MS *m*/*z* 537 (100, [M^{+} − CH$_3$]); Anal. Calc. for C$_{33}$H$_{46}$O$_2$STi: C, 71.49; H, 8.30. Found: C, 71.74; H, 8.47.

3.6. Ti(tbmp){η^{5}-1,3-(SiMe$_3$)$_2$C$_5$H$_3$}Cl (6)

A solution of tbmpH$_2$ (0.87 g, 2.44 mmol) in hexane (ca. 25 ml) was added to a suspension of NaH (0.12 g, 4.88 mmol) in hexane (ca. 20 ml) and the mixture was stirred for 16 h. A solution of Ti{η^{5}-1,3-(SiMe$_3$)$_2$C$_5$H$_3$}Cl$_3$ (0.89 g, 2.44 mmol) in diethyl ether (ca. 60 ml) was added to the mixture and stirred for 4 h. The resulting solution was filtered and concentrated to ca. 10 ml and cooled to −20°C overnight to afford 0.91 g of a dark red solid. From the mother liquor a second crop was obtained (0.49 g); combined yield 1.40 g (81%): ^{1}H-NMR δ 0.24 (s, 18H, Si(CH$_3$)$_3$), 1.27 (s, 18H, 6-C(CH$_3$)$_3$), 2.24 (s, 6H, 4-CH$_3$), 6.99 (br, 2H, 5-H) overlapping 7.01 (br, 1H, 7-H), 7.24 (br, 2H, 9,10-H) overlapping 7.25 (br, 2H, 3-H); ^{13}C{^{1}H}-NMR δ −0.2 (Si(CH$_3$)$_3$), 20.7 (4-CH$_3$), 30.2 (6-C(*C*H$_3$)$_3$), 35.2 (6-*C*(CH$_3$)$_3$), 128.1 (C-2), 128.5 (C-5), 129.9 (C-4), 130.0 (C-9,10), 131.0 (C-7), 132.4 (C-3), 137.6 (C-8,11), 138.1 (C-6), 166.5 (C-1); EI MS *m*/*z* 648 (100, [M^{+}]), 439 (96, [M^{+}-(SiMe$_3$)$_2$C$_5$H$_3$]); Anal. Calc. for C$_{33}$H$_{49}$ClO$_2$SSi$_2$Ti: C, 61.05; H, 7.61. Found: C, 61.21; H, 7.57.

3.7. Ti(tbmp){η^{5}-1,3-(SiMe$_3$)$_2$C$_5$H$_3$}Me (7)

Following a procedure analogous to that described to prepare **2**, the chloro complex **6** (0.35 g, 0.54 mmol) and methylmagnesium chloride (0.20 ml of a 3 M solution in THF) were reacted to give yellow–red micro-crystals; yield 0.25 g (75%): ^{1}H-NMR δ 0.18 (s, 18H, Si(CH$_3$)$_3$), 1.26 (s, 18H, 6-C(CH$_3$)$_3$), 1.31 (s, 3H, TiCH$_3$), 2.23 (s, 6H, 4-CH$_3$), 6.68 (t, $^{4}J_{HH}$ = 2 Hz, 1H, 7-H), 6.76 (d, $^{4}J_{HH}$ = 2 Hz, 2H, 9,10-H), 6.99 (d, $^{4}J_{HH}$ = 2 Hz, 2H, 5-H), 7.33 (d, $^{4}J_{HH}$ = 2 Hz, 2H, 3-H); ^{13}C{^{1}H}-NMR δ −0.1 (Si(CH$_3$)$_3$), 20.7 (4-CH$_3$), 30.2 (6-C(*C*H$_3$)$_3$), 35.1 (6-*C*(CH$_3$)$_3$), 60.5 (TiCH$_3$), 125.4 (C-9,10), 127.6 (C-2), 128.2 (C-5), 128.5 (C-4), 129.6 (C-8,11), 131.5 (C-7), 132.3 (C-3), 137.3 (C-6), 166.8 (C-1); Anal. Calc. for C$_{34}$H$_{52}$O$_2$SSi$_2$Ti: C, 64.98; H, 8.28. Found: C, 64.94; H, 8.59.

3.8. Ti(tbmp){η^{5}-1,3-(SiMe$_3$)$_2$C$_5$H$_3$}(CH$_2$Ph) (8)

Following a procedure analogous to that described to prepare **3**, the chloro complex **6** (0.35 g, 0.54 mmol) was reacted with benzylmagnesium chloride (0.45 ml of a 1.24 M solution in THF) to give a yellow–brown solid; yield 0.38 g (70%): ^{1}H-NMR δ −0.06 (s, 18H, $Si(CH_3)_3$), 1.32 (s, 18H, 6-$C(CH_3)_3$), 2.18 (s, 6H, 4-CH_3), 3.15 (s, 2H, $TiCH_2$), 6.47 (d, $^{4}J_{HH} = 2$ Hz, 2H, 5-H), 6.96(d, $^{4}J_{HH} = 2$ Hz, 2H, 3-H), 7.02 (t, $^{4}J_{HH} = 2$ Hz, 1H, 7-H), 7.20, 7.24 (br, 2H, C_6H_5), 7.26 (br, 2H, 9,10-H), 7.27 (br, 2H, C_6H_5); $^{13}C\{^{1}H\}$-NMR δ −0.2 ($Si(CH_3)_3$), 20.8 (4-CH_3), 30.2 (6-$C(CH_3)_3$), 35.2 (6-$C(CH_3)_3$), 82.6 ($TiCH_2$), 122.6 (C_6H_5), 125.9 (C-8,11), 126.5, 127.9 (C_6H_5), 128.3 (C-2), 128.5 (C-5), 128.9 (C-4), 129.2 (C-9,10), 131.0 (C-7), 133.4 (C-3), 138.1 (C-6), 153.1 (*ipso* C_6H_5), 166.0 (C-1); EI MS m/z 613 (100, $[M^+ - C_7H_7]$); Anal. Calc. for $C_{40}H_{56}O_2SSi_2Ti$: C, 68.20; H, 7.95. Found: C, 67.90; H, 7.80.

3.9. X-ray crystal structure analysis of **1**

Crystallographic data are summarized in Table 2. Single crystals of **1** were grown from a diethyl ether/hexane solution at −30°C. Data were collected using an ENRAF–Nonius CAD4 diffractometer (λ-scan mode, Mo–K_α radiation, $\lambda = 0.7107$ Å). Data correction for Lorentz polarization and absorption (using Ψ-scans) was carried out using the program system MOLEN [21a]. From 7400 measured reflections, 6993 were independent. The structure was solved using direct methods (SHELXS-86) [21b] and difference Fourier syntheses and refined by full-matrix least-squares against all F_o^2 data (SHELXL-93) [21c] (473 parameters). The non-hydrogen atoms of the complex were refined with anisotropic displacement parameters and the hydrogen atoms were refined with isotropic displacement parameters. The crystal structure shows diethyl ether included around a centre of inversion. Split positions of the severely disordered molecule could be resolved and refined with isotropic displacement parameters. Hydrogen atoms of this molecule were not included in the structure factor calculation. The refinement converged with $R = 0.0448$, $wR_2 = 0.1110$ for all observed F_o data, goodness-of-fit 1.078.

Table 2
Crystallographic data for Ti(tbmp)(η^5-C_5H_5)Cl (**1**)

Empirical formula	$C_{27}H_{33}ClO_2STi \cdot 0.5C_4H_{10}O$
f_w	542.00
Crystal colour	Red
Crystal size (mm)	0.51 × 0.51 × 0.83
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
a (Å)	9.715(3)
b (Å)	12.834(3)
c (Å)	12.951(4)
α (°)	67.95(2)
β (°)	83.73(2)
γ (°)	76.20(2)
V (Å^3)	1453.1(7)
Z	2
D_{calc} (mg m^{-3})	1.239
Absorption coefficient (mm^{-1})	0.483
F(000)	574
Temperature (K)	296(2)
θ range (°)	3 to 28
Index ranges	$0 \le h \le 12$; $-16 \le k \le 16$; $-17 \le l \le 17$
Reflections measured	7400
Independent reflections	6993 ($R_{int} = 0.0197$)
Observed reflections	5280
Final R indices R_1, wR_2 [$I \ge 2\sigma$(I)]	0.0448, 0.1110
Final R indices R_1, wR_2 (all data)	0.0670, 0.1330
Goodness-of-fit	1.078
Largest e_{max}, e_{min} (e Å^{-3})	0.348 and −0.273

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 154412. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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