

Regioselective formation of [2-(η^5 -cyclopentadienyl)-2-fluorenylpropane]-titanium complexes: precursors, synthesis, structure and reactivity

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Abstract

The 2-cyclopentadienyl-2-fluorenylpropane ligand has been converted into the monometalated derivatives $M[\text{CMe}_2(\text{C}_5\text{H}_4)(\text{C}_{13}\text{H}_9)]$ ($M = \text{Li}, \text{Tl}$), and $\text{CMe}_2[\text{C}_5\text{H}_4(\text{SiMe}_3)(\text{C}_{13}\text{H}_9)]$. These alkylating reagents have been characterized, and used to synthesize a new series of organotitanium (IV) complexes. The trimethylsilyl derivative was treated with TiCl_4 to give the monocyclopentadienyl compound $[\text{Ti}\{\text{CMe}_2(\eta^5\text{-C}_5\text{H}_4)(\text{C}_{13}\text{H}_9)\}\text{Cl}_3]$. Reaction of the thallium derivative with $[\text{Ti}(\eta^5\text{-C}_5\text{R}_5)\text{Cl}_3]$ afforded the ‘mixed-ring’ dicyclopentadienyl complexes $[\text{Ti}\{\text{CMe}_2(\eta^5\text{-C}_5\text{H}_4)(\text{C}_{13}\text{H}_9)\}(\eta^5\text{-C}_5\text{R}_5)\text{Cl}_2]$ ($\text{R} = \text{H}, \text{Me}$), whereas the reaction of TiCl_4 with two equivalents of the lithium compound led to the dicyclopentadienyl complex $[\text{Ti}\{\text{CMe}_2(\eta^5\text{-C}_5\text{H}_4)(\text{C}_{13}\text{H}_9)\}_2\text{Cl}_2]$. The monocyclopentadienyl compound $[\text{Ti}\{\text{CMe}_2(\eta^5\text{-C}_5\text{H}_4)(\text{C}_{13}\text{H}_9)\}\text{Cl}_3]$ was readily hydrolyzed to give $[\text{Ti}\{\text{CMe}_2(\eta^5\text{-C}_5\text{H}_4)(\text{C}_{13}\text{H}_9)\}\text{Cl}_2(\mu\text{-O})]$ in wet acetone (0.5% H_2O). The dicyclopentadienyl derivative $[\text{Ti}\{\text{CMe}_2(\eta^5\text{-C}_5\text{H}_4)(\text{C}_{13}\text{H}_9)\}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2]$ was further converted into $[\text{Ti}\{\text{CMe}_2(\eta^5\text{-C}_5\text{H}_4)(\text{C}_{13}\text{H}_9)\}(\eta^5\text{-C}_5\text{Me}_5)\text{Me}_2]$ by alkylation with LiMe . Structural data of the titanium complexes demonstrate the η^5 -coordination of the cyclopentadienyl ring of the ancillary ligand, whereas the fluorenyl ring is not coordinated to the metal center. This mode of coordination is confirmed by the X-ray crystal structure analysis of $[\text{Ti}\{\text{CMe}_2(\eta^5\text{-C}_5\text{H}_4)(\text{C}_{13}\text{H}_9)\}_2\text{Cl}_2]$. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Bridged ligands; Cyclopentadienyl; Fluorenyl; Titanium complexes

1. Introduction

In recent years, the study of bridged dicyclopentadienyl group 4 transition metal complexes has become an important area of research. The so-called *ansa*-metallocene derivatives, where the bridged ligand coordinates to a metal center as a chelating group, have attracted attention as Ziegler–Natta catalysts for the stereoregular polymerization of α -olefins [1], and as stereoselective catalysts or reagents for asymmetric induced processes [2]. There is also increasing interest in the use of these

didentate dicyclopentadienyl ligands for the synthesis of homo- and hetero-dinuclear complexes, where the ancillary ligand is in a bridging coordination mode [3–6]. Among the features of this type of compound, the stability of the dicyclopentadienyl framework strongly bonded to two close metal centers confers a potential cooperative effect on the molecule that could be useful during catalytic reactions. A considerable number of group 4 homodimetallic compounds have been reported [4,5]. However, the synthesis of heterodinuclear compounds containing one (or two) metal center of this group has been limited to the recent development of novel and interesting approaches [6].

The $[\text{CMe}_2(\text{C}_5\text{H}_4)(\text{C}_{13}\text{H}_8)]^{2-}$ dianionic ligand has previously been used for the synthesis of C_s -symmetric

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¹ X-ray diffraction studies.

group 4 *ansa*-metallocenes ([1]b, [7]), and has been found to form tris(cyclopentadienyl)zirconium compounds with unusual *ansa*-ligand coordination [5c, 8]. The synthesis of tris(dimethylamido)[2-(η^5 -cyclopentadienyl)-2-fluorenylpropane]zirconium via amine elimination has very recently been reported [9], and several related compounds containing the 2-(η^5 -cyclopentadienyl)-2-indenylpropane ligand have also been described ([5]b–c, [8,10]).

We are interested in the synthesis of group 4 metal compounds containing bridged dicyclopentadienyl ligands with only one of the rings penta-hapto coordinated, as potential precursors for the synthesis of dinuclear complexes. In the present study, we have concentrated our efforts on the chemistry of the 2-cyclopentadienyl-2-fluorenylpropane ligand [$\text{CMe}_2(\text{C}_5\text{H}_5)(\text{C}_{13}\text{H}_9)$], and make use of the different reactivity of the two five-membered rings to synthesize a series of new [2-(η^5 -cyclopentadienyl)-2-fluorenylpropane]titanium complexes.

2. Results and discussion

2.1. Synthesis of alkylating reagents

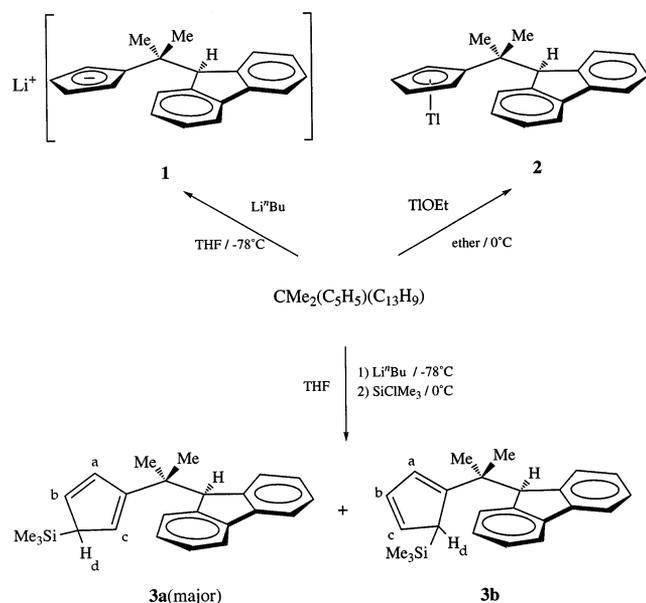
Reaction of [$\text{CMe}_2(\text{C}_5\text{H}_5)(\text{C}_{13}\text{H}_9)$] with one equiv of Li^nBu in THF causes the quantitative formation of compound **1** (Scheme 1). A THF adduct (see Section 4) of this lithium salt is isolated as a highly air-sensitive red solid, soluble in aromatic solvents and THF. The remarkable feature in the $^1\text{H-NMR}$ spectrum of **1** is the presence of two virtual triplets (δ 5.95 and 6.11) for the AA'BB' spin system corresponding to the C_5H_4 -frag-

ment, together with a singlet for the 9-fluorenyl proton (δ 4.36). This pattern clearly indicates the regioselective deprotonation of the cyclopentadienyl group of the starting ligand as a result of the different acidity of the allylic protons of each five-membered ring ($\text{p}K_a \approx 15$ and 22, for cyclopentadiene and fluorene, respectively [11]).

Treatment of [$\text{CMe}_2(\text{C}_5\text{H}_5)(\text{C}_{13}\text{H}_9)$] with one equiv of TIOEt in diethyl ether affords compound **2** as an air-sensitive pale-yellow powder (Scheme 1). Unlike $\text{Ti}(\text{C}_5\text{H}_5)_3$, compound **2** is soluble in aromatic solvents, allowing its study by NMR spectroscopy. The NMR data for **2** are also consistent with the regioselective metallation of the cyclopentadienyl ring. The $^1\text{H-NMR}$ spectrum in C_6D_6 shows the 9-fluorenyl proton as a singlet (δ 4.16), and the $\text{Ti}(\text{C}_5\text{H}_4)$ -group as an AA'BB'X spin system (X = Ti, two doublets of virtual triplets at δ 5.90 and 5.96) with $^2J_{\text{H-Ti}} = 90$ and 83 Hz. The $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **2** also shows $^{13}\text{C-}^{203,205}\text{Ti}$ couplings for the substituted cyclopentadienyl ring with values of $^1J_{\text{C-Ti}} = 65, 39$ and 86 (C_{ipso}) Hz (see Section 4). $^1\text{H-}$ and $^{13}\text{C-}^{203,205}\text{Ti}$ coupling constants have rarely been observed for soluble substituted cyclopentadienylthallium compounds, and some authors have related its occurrence to an enforced covalency of the metal-ring interaction in the corresponding compound, resulting in a decreased tendency for molecular aggregation [12]. For instance, these coupling constants are observed only for the first compound of the series [$\text{Ti}(\text{C}_5\text{H}_2\text{R}_3)$], [$\text{Ti}(\text{C}_5\text{H}_3\text{R}_2)$] $_6$ and [$\text{Ti}(\text{C}_5\text{H}_4\text{R})$] $_8$ (R = SiMe_3) ([12]c), and this has been found to be a monomer in solution with covalent Ti-ring bonding ([12]a). Accordingly, and in contrast to the unsubstituted $\text{Ti}(\text{C}_5\text{H}_5)_3$, a high covalent character can be proposed for **2**, which presumably is a monomeric species in solution due to the presence of the bulky substituent.

Stepwise reaction of [$\text{CMe}_2(\text{C}_5\text{H}_5)(\text{C}_{13}\text{H}_9)$] with one equiv of Li^nBu and in situ treatment of **1** with SiClMe_3 in THF gives the silyl derivative **3** as a white-yellowish solid. Examination of the $^1\text{H-NMR}$ of **3** reveals the crude product to be a mixture of only two isomers, **3a** and **3b** (Scheme 1) in a 9:1 ratio. Isomer **3a** is isolated pure by fractional recrystallization from a pentane solution as a white solid (see Section 4), and its $^1\text{H-NMR}$ spectrum remains unchanged in samples stored for several days at r.t.

It is well-known that sigmatropic H- and Me_3Si -rearrangements in cyclopentadienyltrimethylsilyl compounds result in mixtures of isomers in equilibrium. In particular, in compounds of the type $\text{C}_5\text{H}_4(\text{R})\text{SiMe}_3$ (R nonmigrating group) only 3 of 11 possible isomers, **a–c** in Fig. 1, contribute to the equilibrium at r.t., with relative equilibrium concentrations $\mathbf{a} > \mathbf{b} \gg \mathbf{c}$ due to steric requirements [13]. Moreover, the bulky ligand $\text{R} = -\text{CPh}_3$ has been found to prevent the rearrangements between these isomers, where the only exchange



Scheme 1.

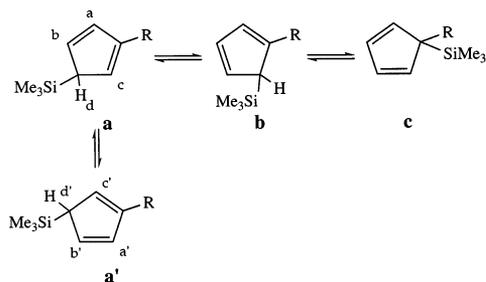


Fig. 1. Sigmatropic Me_3Si -rearrangements in compounds of the type $\text{C}_5\text{H}_4(\text{R})\text{SiMe}_3$.

mechanism corresponds to the degenerate process $\mathbf{a} \rightleftharpoons \mathbf{a}'$ [14] (see Fig. 1). This seems to be the case for **3**; the exchange process between **3a** and **3b** must be very slow at r.t., as indicated by the isolation of pure **3a**, and isomer **3a** predominates whereas the geminal isomer **3c** is not detected in the mixture by $^1\text{H-NMR}$. Furthermore, in a $\{^1\text{H}-^1\text{H}\}$ decoupling experiment carried out to clarify the structure of **3a**, together with the corresponding decouplings, saturation of H_c (see labeling in Fig. 1) showed an important decrease in the intensity (ca. -85%) of the doublet for H_a . This effect could be the result of a slow exchange process between the enantiomers **3a** and **3a'**, in which H_a and H_c are converted respectively (H'_c and H'_a).

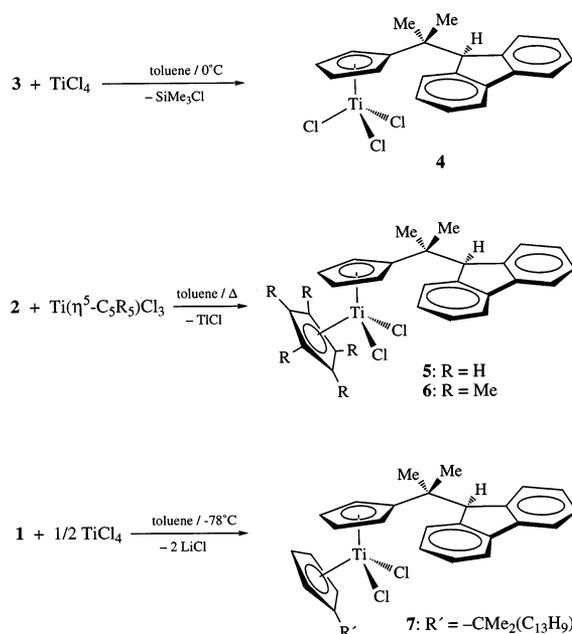
2.2. Synthesis of titanium compounds

Several approaches have been found to be useful for the synthesis of group 4 mono- and di-cyclopentadienyl compounds. However, some of them particularly apply depending on the target product. For instance, the reaction of TiCl_4 with cyclopentadienyltrimethylsilyl derivatives is an efficient method for the synthesis of monocyclopentadienyl complexes [15]. Further reaction with a thallium derivative of a different cyclopentadienyl ligand leads to almost quantitative formation of 'mixed-ring' compounds of titanium [16]; whereas the reaction of TiCl_4 with two equivalents of an alkali metal cyclopentadienyl salt is the most commonly used procedure for the synthesis of di(cyclopentadienyl)dichlorotitanium complexes [17].

Following the above considerations, compounds **4–7** are readily prepared from precursors **1–3** (Scheme 2). Addition of the mixture of isomers **3** to a toluene solution of TiCl_4 gives the monocyclopentadienyl complex **4** in good yield as a moisture-sensitive (vide infra) yellow solid; reaction of **2** with either $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_3]$ or $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_3]$ in toluene, affords the dicyclopentadienyl complexes **5** and **6**, respectively, as air-stable red solids, and treatment of TiCl_4 in toluene with two

equivalents of **1**, yields the dicyclopentadienyl compound **7** as an air-stable red solid. The solubility of these compounds follows the trends $\mathbf{5} < \mathbf{7} < \mathbf{6} \cong \mathbf{4}$, and alkanes $<$ toluene $<$ acetone $\cong \text{CH}_2\text{Cl}_2$ as solvents. In contrast to **4** (formally $12 e^-$ complex), the less electron deficient dicyclopentadienyl complexes **5–7** ($16 e^-$) are air-stable in solution, and can be recrystallized in wet acetone without decomposition. The $^1\text{H-NMR}$ spectra of **4–7** show the characteristic $\text{AA}'\text{BB}'$ spin system for the substituted cyclopentadienyl ring, together with a singlet for the 9-fluorenyl proton, at normal ranges. This spin system is recorded as two virtual triplets for **4**, **6** and **7**, whereas for **5** it is observed as a multiplet due to a smaller difference between $\delta\text{H}_{\text{AA}'}$ and $\delta\text{H}_{\text{BB}'}$. Computer analysis of the spectrum of **5** at 500 MHz allows the calculation of this difference as well as the corresponding coupling constants ($\Delta\nu = 6.27$ Hz; $J_{\text{AA}'} = 1.98$, $J_{\text{AB}} = 2.45$, $J_{\text{AB}'} = 2.96$ and $J_{\text{BB}'} = 1.82$ Hz). The $^{13}\text{C-NMR}$ spectroscopic data of **4–7** are also consistent with the proposed structures (see Section 4).

The single-crystal X-ray structure analysis of **7** confirms the mode of coordination of the $[\text{CMe}_2(\eta^5\text{-C}_5\text{H}_4)(\text{C}_{13}\text{H}_9)]$ ligand in the titanium compounds. Fig. 2 gives an ORTEP view of the structure of **7** together with the atom labeling, while Table 1 presents selected bond distances and angles, and Table 2 summarizes crystal data and structure refinement. In the solid the molecule is C_2 -symmetric. The geometry around Ti, as defined by the centroids of the cyclopentadienyl rings and the Cl atoms, is roughly tetrahedral, the angle



Scheme 2.

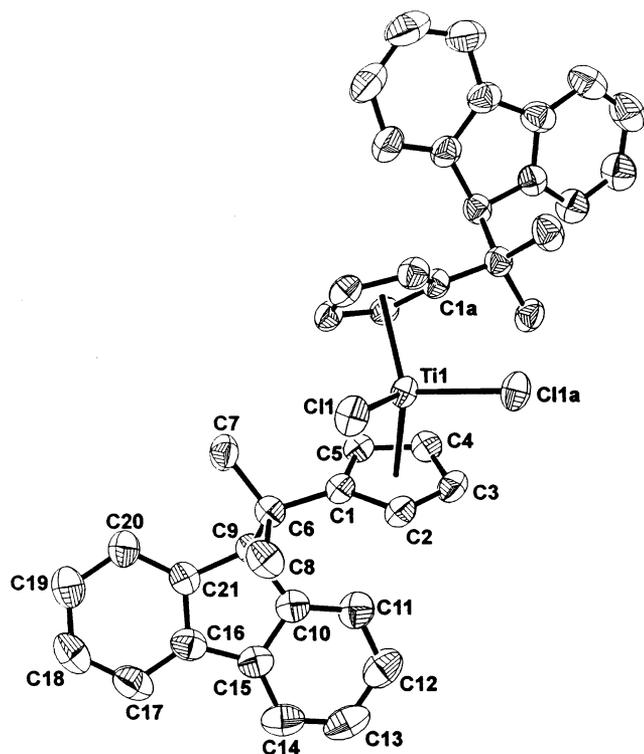


Fig. 2. Molecular structure of 7.

between centroids being much larger (131.4°) than the angle between the Cl atoms (92.4°). These angles are slightly larger and slightly closer respectively than those observed for the unsubstituted $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ (131.0 and 94.6°) [17], and similar to those found for $\text{C}_5\text{H}_4\text{Bu}_2\text{Cl}_2$ [18]. There is some spread in the Ti–C(ring) bond lengths, with the longest distance for the substituted C(1) ($2.508(4)$ Å). The average C–C distance in the ring is 1.406 Å. Possibly for steric reasons, the fluorenyl groups are located away from the metal center, and both substituents of the cyclopentadienyl rings are disposed *anti* to one another, with a torsion angle C(6)–C(1)⋯C(1a)–C(6a) of 164.1° . The shortest intermolecular distance between the Cl atom of one molecule and the hydrogen on C(5) of the nearest molecule in the unit cell is $2.654(4)$ Å. This value might indicate an intermolecular hydrogen bonding interaction in the solid state, which might be

Table 1
Selected bond lengths (Å) and angles ($^\circ$) for complex 7^a

Ti–Cl(1)	2.372(1)	Ti–C(5)	2.391(4)
Ti–C(1)	2.508(4)	Ti–Cp	2.093
Ti–C(2)	2.447(4)		
Ti–C(3)	2.387(4)	Cl(1)–Ti–Cl(1a)	92.4
Ti–C(4)	2.321(4)	Cp–Ti–Cp	113.4
		C(1)–C(6)–C(9)	105.9(9)

^a Cp is the center of the cyclopentadienyl ring.

Table 2
Crystal data and structure refinement for 7

Empirical formula	$\text{C}_{42}\text{H}_{38}\text{Cl}_2\text{Ti}$
Formula weight	661.52
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	14.665(3)
b (Å)	6.568(1)
c (Å)	17.816(4)
β ($^\circ$)	102.46(3)
Unit cell volume (Å ³)	1675.6(6)
Z	2
Density _{calcd} (g cm ⁻³)	1.311
Absorption coefficient (mm ⁻¹)	0.444
$F(000)$	692
Reflections collected	3867
Independent reflections	3656 ($R_{\text{int}} = 0.0225$)
Data/restraints/parameters	3648/0/208
Goodness-of-fit on F^2	0.906
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0484$, $wR_2 = 0.1371$
R indices (all data)	$R_1 = 0.1318$, $wR_2 = 0.2179$
Weighting scheme	Calc. $w = 1/[\sigma^2(F_o^2) + (0.1239P)^2 + 3.0612P]$ where $P = (F_o^2 + 2F_c^2)/3$

also favored by face to face aromatic interactions of the fluorenyl rings [19] (see Fig. 3).

Complexes such as $\text{Ti}(\eta^5\text{-C}_5\text{R}_5)\text{Cl}_3$ ($\text{R} = \text{H}, \text{Me}$) have been found to be moisture-sensitive, and their product of hydrolysis to depend upon reaction conditions [20]. This is also observed for the monocyclopentadienyl compound **4**. Stirring a sample of **4** in wet acetone (0.5% H_2O) leads to the formation of the μ -oxo compound **8** in good yield (Scheme 3). However, reaction with one equivalent of H_2O in dry CH_2Cl_2 in the presence of one equivalent of $t\text{BuNH}_2$ results in a complicated mixture of non characterizable compounds. Complex **8** is obtained as a crystalline yellow solid, slightly soluble in alkanes and soluble in common solvents. The ^1H - and ^{13}C -NMR spectra of **8** show the expected peaks with chemical shifts in the normal range. As observed for **5**, the protons of the C_5H_4 -group (δ 6.62) of the μ -oxo compound **8** are recorded as a multiplet due to a small difference between $\delta\text{H}_{\text{AA}'}$ and $\delta\text{H}_{\text{BB}'}$. Computer analysis of the spectrum of **8** at 500 MHz shows this difference ($\Delta\nu = 4.46$ Hz) to be smaller than that found for **5**, whereas the calculated coupling constants are the same ($J_{\text{AA}'} = 1.98$, $J_{\text{AB}} = 2.45$, $J_{\text{AB}'} = 2.96$ and $J_{\text{BB}'} = 1.82$ Hz). The elemental analysis data confirm the structure of **8**, and exclude compounds of further hydrolysis (e.g. cyclic oligomers of general formula $[\text{Ti}(\eta^5\text{-C}_5\text{R}_5)\text{Cl}(\mu\text{-O})]_n$, $n = 2, 3, 4$) well-known for compounds such as $[\text{Ti}(\eta^5\text{-C}_5\text{R}_5)\text{Cl}_3]$ ($\text{R} = \text{H}, \text{Me}$) [20]. The infrared spectrum of **8** shows the $\nu_{\text{Ti-O-Ti}}$ absorption at 773 cm^{-1} .

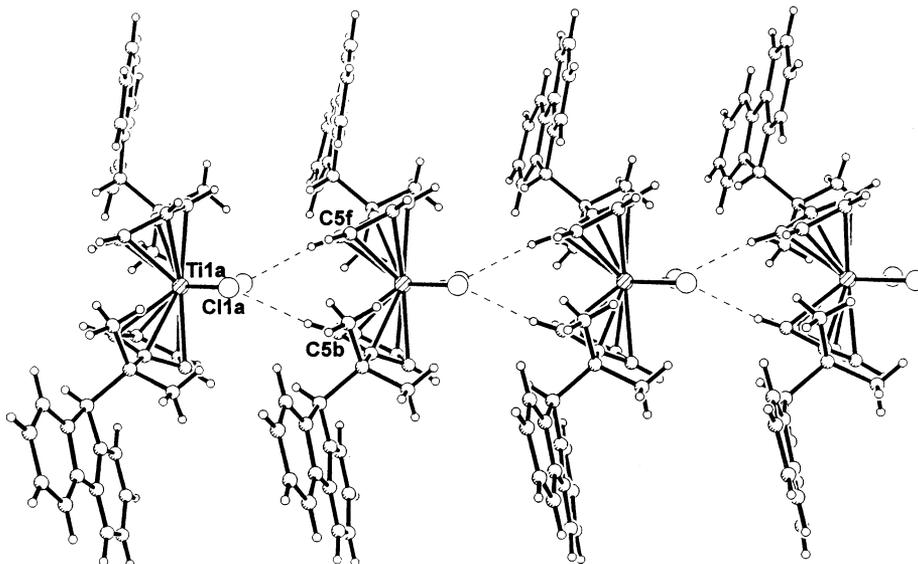


Fig. 3. Packing of the dicyclopentadienyl compound 7.

Reaction of **6** with two equivalents of LiMe, in hexane at low temperature, leads to a thermally-stable moisture-sensitive orange microcrystalline solid, characterized as the dimethyl compound **9** (Scheme 3). After purification, compound **9** is obtained in good yield, and under the reaction conditions neither the evolution of methane nor the presence of a lithium salt from the deprotonation of the fluorenyl ring is detected. This means that the process is chemo-selective since the precursor **6** undergoes the alkylation of the Ti–Cl bonds rather than the metallation of the fluorenyl ring. The ^1H - and ^{13}C -NMR spectra of **9** are fairly similar to the spectra observed for **6** with the addition of the resonances for the methyl groups attached to titanium (^1H : δ -0.22; $^{13}\text{C}\{^1\text{H}\}$: δ 46.8).

The mass spectra and elemental analyses for compounds **2–9** are in agreement with the proposed formulations.

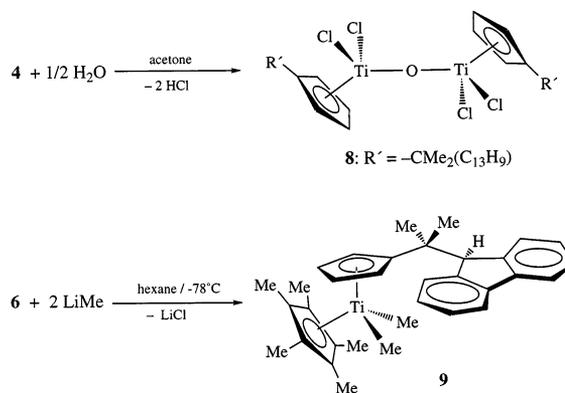
3. Conclusions

The regioselective metallation of the cyclopentadienyl ring of the $[\text{CMe}_2(\text{C}_5\text{H}_5)(\text{C}_{13}\text{H}_9)]$ ligand is readily accessible due to the different acidity of the two five-membered rings. This approach has been applied to synthesize the desired precursors **1–3**, which have been successfully used as intermediates to prepare a series of mono- and di-cyclopentadienyltitanium complexes (**4–7**) and derivatives (**8** and **9**). The common structural feature in the titanium complexes is the η^5 -coordination of the cyclopentadienyl ring of the ancillary ligand to the metal center, whereas the fluorenyl ring remains unchanged.

4. Experimental procedure

4.1. General methods

All operations were performed under an argon atmosphere using Schlenk or dry-box techniques. Argon was deoxygenated with activated BTS catalyst and dried with molecular sieves and P_2O_5 . All common chemicals and solvents were purchased from commercial suppliers and purified as described elsewhere [21]. 6,6-Dimethylfulvene [22], 2-cyclopentadienyl-2-fluorenylpropane [23], $[\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_3]$ ([15]a), and $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_3]$ ([15]b), were prepared according to literature procedures. NMR spectra were recorded on Varian Unity 500+ or Varian Unity VXR-300 NMR spectrometers. Chemical shifts (δ) are reported in ppm referenced to TMS. Infrared spectra were obtained with a Perkin–Elmer Model 883 instrument between 4000 and 200 cm^{-1} . Elemental analyses and mass spectra were performed



Scheme 3.

by the University of Alcalá Microanalytical Laboratories (UCSA) on a Heraeus CHN-O-Rapid microanalyzer and a Hewlett-Packard 5890 mass spectrometer, respectively.

4.2. Isolation of $\text{Li}[\text{CMe}_2(\text{C}_5\text{H}_4)(\text{C}_{13}\text{H}_9)](\text{THF})_{2-3}$ (**1**)

A solution of *n*-butyllithium (16.5 ml, 1.6 M in hexanes) was added dropwise to a THF solution (150 ml) of 2-cyclopentadienyl-2-fluorenylpropane (7.20 g, 26.43 mmol) at -78°C . The reaction mixture was subsequently allowed to warm to r.t. and stirred for an additional 4 h. The solvent was removed under vacuum, and the residue washed with pentane (3×30 ml) to give **1** as a red solid in quantitative yield. This lithium salt was isolated as an adduct with 2.8 equivalents of THF as indicated by $^1\text{H-NMR}$. $^1\text{H-NMR}$ (300 MHz, C_6D_6 , 25°C): $\delta = 1.19$ (m, 11H, THF), 1.41 (s, 6 H, Me_2C), 3.16 (m, 11H, THF), 4.36 (s, 1H, C_{13}H_9 -saturated), 5.95 (t, 2H, C_5H_4), 6.11 (t, 2H, C_5H_4), 7.19 (m, 6H, C_{13}H_9), 7.57 (m, 2H, C_{13}H_9).

4.3. Preparation of $\text{Tl}[\text{CMe}_2(\eta^5\text{-C}_5\text{H}_4)(\text{C}_{13}\text{H}_9)]$ (**2**)

A reaction of TlOEt (1.29 ml, 18.17 mmol) with 2-cyclopentadienyl-2-fluorenylpropane (4.95 g, 18.17 mmol) was carried out in diethyl ether (100 ml) at 0°C . The resulting solution was stirred overnight at r.t.. Removal of the solvent under reduced pressure afforded the thallium salt as a pale-yellow solid which was washed with hexane (3×30 ml). Compound **2** was purified by recrystallization at -40°C from a toluene/hexane solution (2:1), and obtained as a beige microcrystalline solid. Yield: 7.48 g (87%). $^1\text{H-NMR}$ (500 MHz, C_6D_6 , 25°C): $\delta = 1.16$ (s, 6H, Me_2C), 4.16 (s, 1H, C_{13}H_9 -saturated), 5.90 (dt, $^2J(\text{H,Tl}) = 90$ Hz, 2H, C_5H_4), 5.96 (dt, $^2J(\text{H,Tl}) = 83$ Hz, 2H, C_5H_4), 7.14, 7.23 and 7.60 ($3 \times$ m, 8H, C_{13}H_9); $^{13}\text{C}\{^1\text{H}\}$ -NMR (125 MHz, C_6D_6 , 25°C): $\delta = 28.8$ (d, $^3J(\text{C,Tl}) = 43$ Hz, Me_2C), 38.9 (d, $^2J(\text{C,Tl}) = 17$ Hz, Me_2C), 60.5 (d, $^3J(\text{C,Tl}) = 16$ Hz, C_{13}H_9 -saturated), 105.1 (d, $^1J(\text{C,Tl}) = 65$ Hz, C_5H_4), 107.3 (d, $^1J(\text{C,Tl}) = 39$ Hz, C_5H_4), 119.5, 126.3, 127.3 and 146.8 ($4 \times$ s, C_{13}H_9), 140.3 (d, $^1J(\text{C,Tl}) = 86$ Hz, C_5H_4 -*ipso*), 142.6 and 142.7 ($2 \times$ s, C_{13}H_9 -quaternaries). MS (70 eV, EI): m/z (%) = 476 (0.4) [$^{205}\text{M}^+$], 311 (10.1) [$^{205}\text{M}^+ - \text{C}_{13}\text{H}_9$], 309 (4.3) [$^{203}\text{M}^+ - \text{C}_{13}\text{H}_9$], 205 (100) [$^{205}\text{Tl}^+$], 203 (41.9) [$^{203}\text{Tl}^+$], 165 (30.8) [$\text{C}_{13}\text{H}_9^+$]. Anal. Found: C, 52.93; H, 3.96. $\text{C}_{21}\text{H}_{19}\text{Tl}$. Calc.: C, 53.02; H, 4.03.

4.4. Preparation of $\text{CMe}_2[\text{C}_5\text{H}_4(\text{SiMe}_3)](\text{C}_{13}\text{H}_9)$ (**3**)

A solution of the lithium salt **1** (18.35 mmol, vide supra) was prepared in THF (100 ml), and in situ reacted with SiMe_3Cl (2.8 ml, 22.06 mmol, 20% in excess) at -78°C . After stirring overnight at r.t., the

volatiles were evaporated and the residue was extracted with pentane (3×50 ml) to give **3** as a mixture of isomers **3a** and **3b** (9:1) as a yellowish solid. Recrystallization from a pentane solution (100 ml) afforded two crops of pure **3a** as a white solid (4.48 g, 71%), whereas removal of the solvent from the mother liquor still gave a mixture of **3a** and **3b** (1:1) as a yellowish sticky solid. Combined Yield: 5.69 g (90%).

3a: $^1\text{H-NMR}$ (500 MHz, CDCl_3 , 25°C): for assignments see Scheme 1, $\delta = -0.01$ (s, 9H, Me_3Si), 0.67 (s, 3H, Me_2C), 1.42 (s, 3H, Me_2C), 3.35 (bs, 1H, $\text{C}_5\text{H}_4 - \text{H}_a$), 4.22 (s, 1H, C_{13}H_9 -saturated), 5.98 (bd, $J_{bc} = 1.5$ Hz, 1H, $\text{C}_5\text{H}_4 - \text{H}_c$), 6.60 (bdd, $J_{ab} = 5.0$ Hz, $J_{bc} = 1.5$ Hz, 1H, $\text{C}_5\text{H}_4 - \text{H}_b$), 6.89 (bd, $J_{ab} = 5.0$ Hz, 1H, $\text{C}_5\text{H}_4 - \text{H}_a$), 6.80, 7.56, 7.66, and 7.71 ($4 \times$ d, 4H, C_{13}H_9), 7.02, 7.21, 7.24 and 7.32 ($4 \times$ m, 4H, C_{13}H_9). MS (70 eV, EI): m/z (%) = 344 (0.5) [M^+], 179 (31.8) [$\text{M}^+ - \text{C}_{13}\text{H}_9$], 165 (19.7) [$\text{C}_{13}\text{H}_9^+$], 106 (2.0) [$\text{Me}_2\text{C}(\text{C}_5\text{H}_4)^+$], 73 (100) [SiMe_3^+]. Anal. Found: C, 83.48; H, 8.10. $\text{C}_{24}\text{H}_{28}\text{Si}$. Calc.: C, 83.66; H, 8.19.

3b: $^1\text{H-NMR}$ (300 MHz, CDCl_3 , 25°C): for assignments see Scheme 1, $\delta = -0.03$ (s, 9H, Me_3Si), 1.15 (s, 3H, Me_2C), 2.17 (s, 3H, Me_2C), 3.73 (m, 1H, $\text{C}_5\text{H}_4 - \text{H}_a$), 4.29 (s, 1H, C_{13}H_9 -saturated), 6.06 (dd, $J_{ab} = 2.2$ Hz, $J_{ac} = 1.5$ Hz, 1H, $\text{C}_5\text{H}_4 - \text{H}_a$), 6.50 (dd, $J_{ab} = 2.2$ Hz, $J_{bc} = 4.5$ Hz, 1H, $\text{C}_5\text{H}_4 - \text{H}_b$), 6.76 (dd, $J_{ac} = 1.5$ Hz, $J_{bc} = 4.5$ Hz, 1H, $\text{C}_5\text{H}_4 - \text{H}_c$), (C_{13}H_9 obscured by resonances of **3a**).

4.5. Preparation of $[\text{Ti}\{\text{CMe}_2(\eta^5\text{-C}_5\text{H}_4)(\text{C}_{13}\text{H}_9)\}\text{Cl}_3]$ (**4**)

A solution of **3** (1.60 g, 4.64 mmol) in toluene (25 ml) was slowly added to a solution of TiCl_4 (0.51 ml, 4.64 mmol) in toluene (50 ml) at 0°C , and the mixture stirred at r.t. overnight. Filtration and removal of the solvent, followed by recrystallization from CH_2Cl_2 , afforded **4** as yellow microcrystalline solid. Yield: 1.34 g (68%). $^1\text{H-NMR}$ (300 MHz, CDCl_3 , 25°C): $\delta = 1.61$ (s, 6H, Me_2C), 3.96 (s, 1H, C_{13}H_9 -saturated), 6.55 (t, 2H, C_5H_4), 6.63 (t, 2H, C_5H_4), 7.22 (m, 4H, C_{13}H_9), 7.31 (m, 2H, C_{13}H_9), 7.56 (d, 2H, C_{13}H_9); $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, CDCl_3 , 25°C): $\delta = 25.9$ (Me_2C), 41.7 (Me_2C), 60.2 (C_{13}H_9 -saturated), 121.9 (C_5H_4), 122.7 (C_5H_4), 119.7, 126.2 and 127.9 (C_{13}H_9), 141.9 and 143.9 (C_{13}H_9 -quaternaries), 151.5 (C_5H_4 -*ipso*). MS (70 eV, EI): m/z (%) = 426/424 (0.2/0.2) [M^+], 261/259 (4.3/4.4) [$\text{M}^+ - \text{C}_{13}\text{H}_9$], 226/224 (1.6/2.8) [$\text{M}^+ - \text{C}_{13}\text{H}_9\text{Cl}$], 165 (100) [$\text{C}_{13}\text{H}_9^+$], 106 (3.5) [$\text{Me}_2\text{C}(\text{C}_5\text{H}_4)^+$]. Anal. Found: C, 59.29; H, 4.51. $\text{C}_{21}\text{H}_{19}\text{TiCl}_3$. Calc.: C, 59.26; H, 4.50.

4.6. Preparation of $[\text{Ti}\{\text{CMe}_2(\eta^5\text{-C}_5\text{H}_4)(\text{C}_{13}\text{H}_9)\}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2]$ (**5**)

A suspension of **2** (3.27 g, 6.87 mmol) in toluene (75 ml) was treated with $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_3]$ (1.51 g, 6.87 mmol) and refluxed for 2 h. The toluene was then

removed under vacuum, and the residue was transferred to a Soxhlet apparatus and extracted into CH_2Cl_2 (250 ml) to give **5** as an air stable red microcrystalline solid, which was recrystallized in CH_2Cl_2 . Yield: 2.48 g (79%). $^1\text{H-NMR}$ (500 MHz, CDCl_3 , 25°C): $\delta = 1.50$ (s, 6H, Me_2C), 3.89 (s, 1H, C_{13}H_9 -saturated), 6.30 (m, 4H, C_5H_4), 6.50 (s, 5H, C_5H_5), 7.05 and 7.58 (2 \times d, 2 \times 2H, C_{13}H_9), 7.13 and 7.29 (2 \times t, 2 \times 2H, C_{13}H_9); $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, CDCl_3 , 25°C): $\delta = 25.2$ (Me_2C), 41.9 (Me_2C), 61.3 (C_{13}H_9 -saturated), 116.3 (C_5H_4), 122.0 (C_5H_4), 120.1 (C_5H_5), 119.4, 126.0, 126.4 and 127.4 (C_{13}H_9), 142.0 and 144.5 (C_{13}H_9 -quaternaries), 145.3 (C_5H_4 -ipso). MS (70 eV, EI): m/z (%) = 419 (1.2) [$\text{M}^+ - \text{Cl}$], 289 (2.7) [$\text{M}^+ - \text{C}_{13}\text{H}_9$], 165 (100) [$\text{C}_{13}\text{H}_9^+$], 65 (10.6) [C_5H_5^+]. Anal. Found: C, 68.62; H, 5.46. $\text{C}_{26}\text{H}_{24}\text{TiCl}_2$. Calc.: C, 68.59; H, 5.31.

4.7. Preparation of $[\text{Ti}\{\text{CMe}_2(\eta^5\text{-C}_5\text{H}_4)(\text{C}_{13}\text{H}_9)\}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2]$ (**6**)

A suspension of **2** (2.49 g, 5.23 mmol) in toluene (75 ml) was treated with $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_3]$ (1.52 g, 5.23 mmol) and refluxed overnight. The solution was cooled and the TiCl byproduct was filtered out. Concentration of the filtrate afforded **6** as an air stable dark-red crystalline solid, which was recrystallized in CH_2Cl_2 . Yield: 1.94 g (71%). $^1\text{H-NMR}$ (500 MHz, CDCl_3 , 25°C): $\delta = 1.55$ (s, 6H, Me_2C), 2.00 (s, 15H, C_5Me_5), 3.92 (s, 1H, C_{13}H_9 -saturated), 5.78 (t, 2H, C_5H_4), 6.09 (t, 2H, C_5H_4), 7.01 and 7.59 (2 \times d, 2 \times 2H, C_{13}H_9), 7.11 and 7.27 (2 \times t, 2 \times 2H, C_{13}H_9); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , 25°C): $\delta = 13.5$ (q, $^1\text{J}(\text{C,H}) = 128$ Hz, C_5Me_5), 24.5 (q, $^1\text{J}(\text{C,H}) = 127$ Hz, Me_2C), 41.9 (s, Me_2C), 61.5 (d, $^1\text{J}(\text{C,H}) = 133$ Hz, C_{13}H_9 -saturated), 111.5 (dm, $^1\text{J}(\text{C,H}) = 174$ Hz, C_5H_4), 125.7 (dm, $^1\text{J}(\text{C,H}) = 174$ Hz, C_5H_4), 119.2 and 126.6 (2 \times dd, $^1\text{J}(\text{C,H}) = 157$ Hz, C_{13}H_9), 125.8 and 127.1 (2 \times dm, $^1\text{J}(\text{C,H}) = 160$ Hz, C_{13}H_9), 129.5 (s, C_5Me_5), 142.1 and 145.0 (2 \times s, C_{13}H_9 -quaternaries), 144.5 (s, C_5H_4 -ipso). MS (70 eV, EI): m/z (%) = 489 (1.1) [$\text{M}^+ - \text{Cl}$], 389 (0.6) [$\text{M}^+ - \text{C}_5\text{Me}_5$], 324 (16.0) [$\text{M}^+ - \text{C}_{13}\text{H}_9\text{Cl}$], 253 (27.5) [$\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_2^+$], 165 (100) [$\text{C}_{13}\text{H}_9^+$], 135 (21.7) [C_5Me_5^+]. Anal. Found: C, 70.86; H, 6.63. $\text{C}_{31}\text{H}_{34}\text{TiCl}_2$. Calc.: C, 70.87; H, 6.52.

4.8. Preparation of $[\text{Ti}\{\text{CMe}_2(\eta^5\text{-C}_5\text{H}_4)(\text{C}_{13}\text{H}_9)\}_2\text{Cl}_2]$ (**7**)

A solution of TiCl_4 (0.61 ml, 5.55 mmol) in toluene (25 ml) was added to a suspension of **1** (11.10 mmol) in toluene (100 ml) at -78°C , and stirred overnight at r.t.. The toluene was removed under vacuum, and the residue was extracted into CH_2Cl_2 (2 \times 50ml) to give **7** as an air stable deep-red crystalline solid, which was recrystallized in CH_2Cl_2 . Yield: 1.46 g (40%). $^1\text{H-NMR}$ (300 MHz, CDCl_3 , 25°C): $\delta = 1.48$ (s, 12H, Me_2C), 3.88

(s, 2H, C_{13}H_9 -saturated), 6.23 (t, 4H, C_5H_4), 6.27 (t, 4H, C_5H_4), 7.01 and 7.57 (2 \times d, 2 \times 4H, C_{13}H_9), 7.12 and 7.28 (2 \times t, 2 \times 4H, C_{13}H_9); $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, CDCl_3 , 25°C): $\delta = 25.0$ (Me_2C), 41.9 (Me_2C), 61.4 (C_{13}H_9 -saturated), 115.2 (C_5H_4), 122.9 (C_5H_4), 119.4, 125.9, 126.4 and 127.4 (C_{13}H_9), 142.1 and 144.6 (C_{13}H_9 -quaternaries), 150.0 (C_5H_4 -ipso). MS (70 eV, EI): m/z (%) = 389 (0.2) [$\text{M}^+ - \text{Me}_2\text{C}(\text{C}_5\text{H}_4)\text{C}_{13}\text{H}_9$], 354 (16.4) [$\text{M}^+ - \text{C}_{21}\text{H}_{19}\text{Cl}$], 165 (100) [$\text{C}_{13}\text{H}_9^+$], 106 (3.2) [$\text{Me}_2\text{C}(\text{C}_5\text{H}_4)^+$]. Anal. Found: C, 76.01; H, 5.71. $\text{C}_{42}\text{H}_{38}\text{TiCl}_2$. Calc.: C, 76.25; H, 5.79.

4.9. Preparation of $[\text{Ti}\{\text{CMe}_2(\eta^5\text{-C}_5\text{H}_4)(\text{C}_{13}\text{H}_9)\}\text{Cl}_2]_2(\mu\text{-O})$ (**8**)

A sample of **4** (2.00 g, 4.70 mmol) was dissolved in wet acetone (150 ml, 0.5% H_2O). After being stirred for 8 h at room temperature, the resulting solution was concentrated and cooled (-40°C) to precipitate a yellow solid, which was recrystallized in dry CH_2Cl_2 to give **8** as a yellow crystalline solid. Yield: 1.14 g (61%). $^1\text{H-NMR}$ (500 MHz, CDCl_3 , 25°C): $\delta = 1.51$ (s, 12H, Me_2C), 3.96 (s, 2H, C_{13}H_9 -saturated), 6.62 (m, 8H, C_5H_4), 7.01 and 7.58 (2 \times d, 2 \times 4H, C_{13}H_9), 7.13 and 7.29 (2 \times t, 2 \times 4H, C_{13}H_9); $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, CDCl_3 , 25°C): $\delta = 25.5$ (Me_2C), 41.3 (Me_2C), 60.2 (C_{13}H_9 -saturated), 121.3 (C_5H_4), 121.4 (C_5H_4), 119.6, 126.1, 126.2 and 127.6 (C_{13}H_9), 142.0 and 144.2 (C_{13}H_9 -quaternaries), 149.8 (C_5H_4 -ipso); IR (Nujol): $\nu = 773$ cm^{-1} (Ti–O–Ti). MS (70 eV, EI): m/z (%) = 466 (0.1) [$\text{M}^+ - 2(\text{C}_{13}\text{H}_9)$], 165 (100) [$\text{C}_{13}\text{H}_9^+$]. Anal. Found: C, 63.09; H, 4.76. $\text{C}_{42}\text{H}_{38}\text{Ti}_2\text{Cl}_4\text{O}$. Calc.: C, 63.35; H, 4.81.

4.10. Preparation of $[\text{Ti}\{\text{CMe}_2(\eta^5\text{-C}_5\text{H}_4)(\text{C}_{13}\text{H}_9)\}(\eta^5\text{-C}_5\text{Me}_5)\text{Me}_2]$ (**9**)

A solution of $\text{LiMe}\cdot\text{LiBr}$ (1.1 ml, 1.70 M in diethyl ether, 1.90 mmol) was slowly syringed into a suspension of **6** (0.50 g, 0.95 mmol) in hexane (75 ml) at -78°C . The mixture was allowed to warm up to r.t. and stirred for an additional 8 h. After removal of the volatiles, the residue was extracted with toluene (2 \times 75 ml), and the resulting filtrate was concentrated and cooled (-40°C) to afford **9** as an orange microcrystalline solid. Yield: 0.35 g (76%). $^1\text{H-NMR}$ (300 MHz, C_6D_6 , 25°C): $\delta = -0.22$ (s, 6H, TiMe_2), 1.15 (s, 6H, Me_2C), 1.67 (s, 15H, C_5Me_5), 3.98 (s, 1H, C_{13}H_9 -saturated), 5.34 (t, 2H, C_5H_4), 5.78 (t, 2H, C_5H_4), 7.10 and 7.20 (2 \times d, 2 \times 2H, C_{13}H_9), 7.28 and 7.62 (2 \times t, 2 \times 2H, C_{13}H_9); $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, C_6D_6 , 25°C): $\delta = 12.3$ (C_5Me_5), 24.4 (Me_2C), 41.2 (Me_2C), 46.8 (TiMe_2), 63.0 (C_{13}H_9 -saturated), 112.8 (C_5H_4), 126.2 (C_5H_4), 113.3, 119.7 and 127.4 (C_{13}H_9), 127.5 (C_5Me_5), 140.6 and 142.8 (C_{13}H_9 -quaternaries), 145.6 (C_5H_4 -ipso). MS (70 eV, EI): m/z (%) = 469 (0.2) [$\text{M}^+ - \text{Me}$], 454 (25.4) [$\text{M}^+ - 2\text{Me}$], 349 (0.8) [$\text{M}^+ - \text{C}_5\text{Me}_5$], 319 (30.6) [$\text{M}^+ - \text{C}_{13}\text{H}_9$], 289 (100)

[M⁺-C₁₃H₉ - 2Me], 165 (25.7) [C₁₃H₉⁺]. Anal. Found: C, 81.44; H, 8.16. C₃₃H₄₀Ti. Calc.: C, 81.79; H, 8.32.

4.11. X-ray structural analysis of 7

Single crystals of compound 7 were grown from a dichloromethane solution. The data were collected on an ENRAF NONIUS CAD4 diffractometer. Intensity measurements were performed by $\omega - \theta$ scans in the range $4.68^\circ < 2\theta < 54.00^\circ$ at 19°C on a crystal of dimensions $0.33 \times 0.27 \times 0.23$ mm. Of the 3867 measured reflections, 3656 were independent; largest minimum and maximum in the final difference Fourier synthesis: -0.352 and 0.445 eÅ⁻³, $R_1 = 0.048$ and $wR_2 = 0.137$ (for 2252 reflections with $F > 4\sigma(F)$). The values of R_1 and wR_2 are defined $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; $wR_2 = \{[\Sigma w(F_o^2 - F_c^2)^2] / [\Sigma w(F_o^2)^2]\}^{1/2}$. The structure was solved by direct methods (SHELXS-90) [24] and refined by least-squares against F^2 (SHELXL-93) [25]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were positioned geometrically and refined by using a riding model. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100428. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (UK), (Fax: + 44 1223 336033; e-mail: deposit@chemcryst.cam.ac.uk).

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