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Synthesis and Reactivity of Trimethylsilyl Substituted Mono(cyclopentadienyl)titanium Alkyl Complexes[1]

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Abstract—The preparation of a series of titanium half-sandwich compounds [Ti(η^5-$C_5H_{5-x}(SiMe_3)_xR_3$] (x = 1–3, R = Cl, Me) and their reactivity for propene polymerization is reported. The compounds **1**–**3** polymerize propene, albeit in a much lower activity than the reported [Ti(η^5-$C_5Me_5Me_3$]/$B(C_6F_5)_3$ catalyst. Unlike the reported [Ti(η^5-$C_5Me_5Me_3$]/$B(C_6F_5)_3$ catalyst, the *quasi living* polymerization was not observed. Instead, we observe rather unusual temperature effects when the trityl salt [Ph_3C][$B(C_6F_5)_4$] was used as activator. The activity increases with increasing temperature, whereas when $B(C_6F_5)_3$ is used a decrease is observed The rather broad (>2) PDI indicates multisite catalysts, and ^{13}C-NMR indicates predominantly atactic polypropene. The solid state structure of the hydrolysis product [{Ti(η^5-$C_5H_4(SiMe_3)Cl_2$}O] (**4**) was determined.

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INTRODUCTION

Since Ziegler's discovery some 50 years ago [1] that mixtures of transition metals and alkylaluminum halides polymerize ethene at ambient temperature and pressure, significant efforts have been undertaken to understand the underlying nature of the catalysts. In particular, homogeneous group 4 metallocene compounds have been investigated very thoroughly [2–12]. More recently, late transition metal compounds have become of interest [13–15]. The research interest of group 4 half-sandwich compounds has been fueled again by reports from Hessen et al. that these systems are highly active catalysts for the *trimerization* of ethene [16–18]. To this end, we [19–21] and others [22–28] have reported the formation of arene adducts of cationic group 4 half-sandwich compounds. Whereas these systems are interesting not only for the polymerization of monomers like styrene [29, 30] and isobutene [21, 31], we have also obtained evidence for the *quasi-living* polymerization of propene at ambient temperature, probably the first example of such a polymerization [32, 33]. In our ongoing interest to uncover the underlying principles of cationic base free homogeneous group 4 metal catalysts [19, 20, 34–39], we were interested in whether the reason for that unusual polymerization chemistry lies within the steric or the electronic properties of the ligand. Since five methyl groups on the cyclopentadienyl ligand not only add electron density but also increase the steric environment, we were looking for alternative substituents which are still sterically demanding yet electron neutral. The use of trimethylsilyl groups seem to be advantageous because they are only weak σ-donors and weak π-acceptors [40], thus we hoped to be able to differentiate between the electronic and the steric influence of the substituent. Therefore we prepared a series of trimethylsilyl-substituted titanium half-sandwich compounds [Ti(η^5-$C_5H_{5-x}(SiMe_3)_xR_3$] (x = 1–3, R = Cl, Me) and investigated their polymerization activity. The hydrolysis product [{Ti(η^5-$C_5H_4(SiMe_3)Cl_2$}O] (**4**) was obtained by recrystallization of [Ti(η^5-$C_5H_1(SiMe_3)Cl_3$] (**1a**) from wet pentane and its solid state structure was determined.

RESULTS AND DISCUSSION

Methylation of the compound [Ti(η^5-$C_5H_{5-x}(SiMe_3)_xR_3$] (x = 1, R = Cl **1a**; x = 2, R = Cl **2a**; x = 3, R = Cl **3a**) with the Grignard reagent MeMgBr in diethyl ether afforded the corresponding methyl compounds [Ti(η^5-$C_5H_{5-x}(SiMe_3)_xR_3$] (x = 1, R = Me **1**; x = 2, R = Me **2**; x = 3, R = Me **3**) in good to excellent yields. Compound **1** was obtained as a yellow oil; attempts to obtain a crystalline product failed. It decomposes within days to a dark, highly viscous black oil at ambient temperature even under inert gas (Argon), but can be stored at –30°C for several weeks. Compounds **2** and **3** were obtained as yellow or dark microcystalline solids, respectively. Compound **2** is stable for years at –30°C with little decomposition observed. Satisfactory elemental analysis was difficult to obtain due to the extreme sensitive nature of the compounds. NMR data are presented in Table 1.

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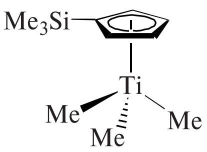
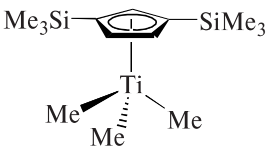
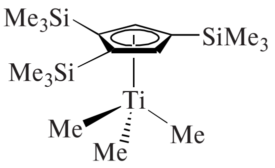
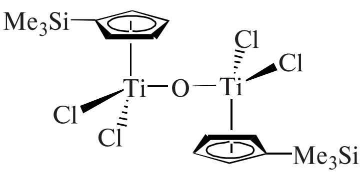
Table 1. NMR Data of compounds **1–4**

Compound	^{1}H δ, (ppm)^{a}	Assignment	^{13}C δ, (ppm)^{b}	Assignment
	0.25 (s, 9H)	$SiCH_3$	−0.4	$SiCH_3$
	1.16 (s, 9H)	$TiCH_3$	62.6	$TiCH_3$
	6.47 (‘m’, 4H)	CpH	117.2	Cp
			127.2	*i*-C–C_5H_5
1				
	0.17 (s, 18H)^{c}	$SiCH_3$	−0.2^{c}	$SiCH_3$
	1.09 (s, 9H)	$TiCH_3$	62.8	$TiCH_3$
	6.55 (s, 3H)	CpH	121.6	Cp
			122.6	Cp
			132.7	*i*-C–C_5H_5
2				
	0.36 (s, 9H)	$SiCH_3$	0.4	$SiCH_3$
	0.47 (s, 18H)	$SiCH_3$	1.2	$SiCH_3$
	1.66 (s, 9H)	$TiCH_3$	64.3	$TiCH_3$
	7.12 (s, 2H)	CpH	130.4	Cp
			134.8	*i*-C–C_5H_5
3				
	0.35 (s, 9H)^{d}	$SiCH_3$	−0.6^{e}	$SiCH_3$
	0.37 (s, 9H)	$SiCH_3$	−0.4	$SiCH_3$
	6.69 (‘t’, 2H)	CpH	121.9	Cp
	6.80 (‘t’, 2H)	CpH	125.1	Cp
	6.93 (‘t’, 2H)	CpH	126.2	Cp
4	7.12 (‘t’, 2H)	CpH	128.6	Cp
			132.8	*i*-C–C_5H_5
			138.9	*i*-C–C_5H_5

Note: ^{a} 300 MHz, $CDCl_3$, 20°C; ^{b} 75.5 MHz $CDCl_3$, 20°C; ^{c} CD_2Cl_2; ^{d} 500 MHz; ^{e} 125 MHz.

Recrystallization of **2** from wet pentane under air afforded the dinuclear compound [{Ti(η^5-$C_5H_4(SiMe_3)Cl_2$}O] (**4**). The solid state structure is shown in Fig. 1. The Ti–O–Ti bond angle of 160.33(19)° and the Ti–Cp_{centr}, bond distances (Cp_{centr}–Ti1: 2.01 Å and Cp_{centr}–Ti_2: 2.02 Å) are similar to those previously reported by Gowik et al. (Ti–O–Ti: 167.5(6)°; Ti–Cp_{centr}: 2.03 Å) [41], but different from those reported by Thewald (Ti–O–Ti: 180°; Ti–Cp_{centr}: 2.01 Å) [42]. The Cp_{centr}–Ti–Ti–Cp_{centr} torsion angle of 90.3° is somewhat smaller than the one reported by Gowik [41] (114.6°) and could be a result of the $SiMe_3$ groups. Selected distances and angles are summarized in Table 2. The presence of 4 triplets in the ^{1}H spectrum for the Cp signals indicated restricted rotation of **4** in solution even at ambient temperature.

Polymerization Studies

Whereas the polymerization of propene with [Ti(η^5-C_5Me_5)Me_3] using $B(C_6F_5)_3$ as the cation generating agent results in the formation of atactic, high molecular weight, elastomeric polypropene with a narrow polydispersity of< 1.5, [32, 33] the compounds **1–3** are far less active by comparison. For example, the polymerization of propene with **1**/$B(C_6F_5)_3$ at 0°C yields a polymer of M_w 31 150 with a polydispersity of 2.4 whereas at 20°C the polydispersity increases to 14.5 with a M_w of 207 450 (cf. Table 3). The reaction with $[Ph_3C]^+[B(C_6F_5)_4]^-$ is even more puzzling. Upon addition of 20 μmol of **1** to a solution of 20 μmol $[Ph_3C]^+[B(C_6F_5)_4]^-$ in 20 ml toluene at 0°C, the reaction mixture is inactive for 100 s, then rapidly undergoes polymerization. The rather broad but unimodal polydispersity (5.0) with a M_w of 268 000, indicates the absence of a single site catalyst. By comparison, compound **2**, when activated with $B(C_6F_5)_3$, is even less active with similar polydispersity. Interestingly, when $[Ph_3C]^+[B(C_6F_5)_4]^-$ is used for activation the activity increases with increasing temperature whereas the $B(C_6F_5)_3$ activated polymerization shows a decrease in activity (see Fig. 2).

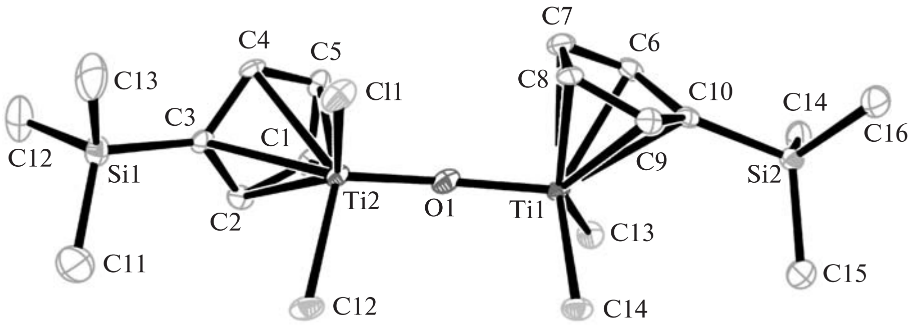


Fig. 1. Solid state structure of **4**.

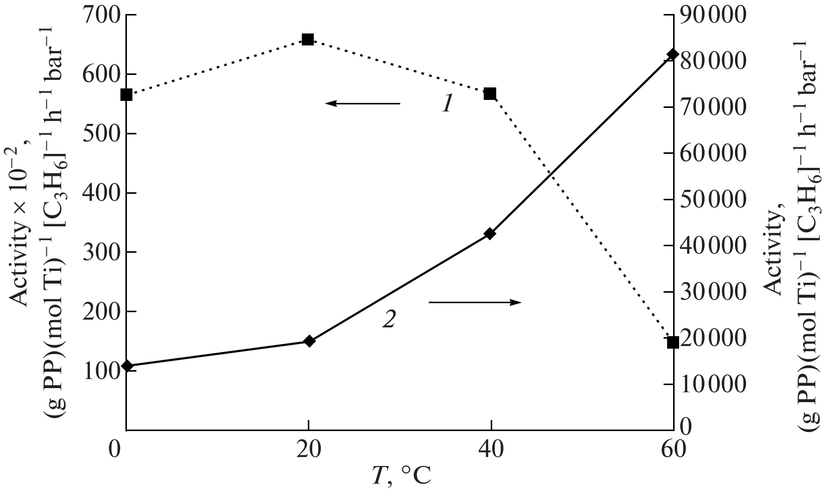


Fig. 2. Propene polymerization with **2**. Activators: (*1*) $B(C_6F_5)_3$ and (*2*) $[Ph_3C]^+[B(C_6H_5)_4]^-$.

Similar observations can be made for compound **3**: at 0°C the GPC curve is trimodal and bimodal at 20°C when activated with $B(C_6F_5)_3$. Again, when $[Ph_3C]^+[B(C_6F_5)_4]^-$ is used for activation increasing temperature leads to increased activity (see Fig. 3). By comparison, compound **2** is slightly more active at low temperatures but shows similar activity as **3** at 60°C when activated with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (see Fig. 4).

^{13}C{^{1}H}-NMR spectra of selected samples indicate the expected predominantly atactic microstructure of the polymer, independent of the temperature and activator. Similar spectra are obtained with the previously reported $[Ti(\eta^5\text{-}C_5Me_5)Me_3]/B(C_6F_5)_3$ mixture.

Table 2

Bond	Bond length, Å	Bond angle	Angle value, deg
Ti1–O1	1.811(3)	Ti2–O1–Ti1	160.33(19)
Ti1–Cl3	2.2529(14)	Cl1–Ti2–O1–Ti1	38.4(6)
Ti1–Cl4	2.2537(14)	Cl2–Ti2–O1–Ti1	–67.8(6)
Ti2–O1	1.799(3)	Cl3–Ti1–O1–Ti2	156.8(5)
Ti2–Cl1	2.2440(14)	Cl4–Ti1–O1–Ti2	51.0(6)
Ti2–Cl2	2.2594(15)	–	–

In summary, **1–3** are significantly less active for the polymerization of propene than $[Ti(\eta^5\text{-}C_5Me_5)Me_3]$ when activated with $B(C_6F_5)_3$. It is obvious that the difference in reactivity must stem from the trimethylsilyl ligand. Indeed, the activity decreases with increasing congestion from the trimethylsilyl group, as indicated from run 1, run 5 and run 13 (Table 3). In the light of recent investigations of trimethylsilyl substituted indenyl-TiCl$_3$ compounds [43], it is tempting to speculate about an interaction between the trimethylsilyl group and the cationic metal centre. For example, Marks reported the formation of a zirconacycle from a *tert*-butyl substituted cationic zirconocene compound (Scheme 1) [44]. Chirik reported the CH activation of Si–CH$_3$ groups of zirconocene hydride compound, yielding a zirconacycle similar to those reported by Marks [45]. It is tempting to propose that similar reactions might occur with the cationic congeners of **1–3** (Scheme 2). These metallacycles could shut down the catalyst very effectively, leaving only a small portion of

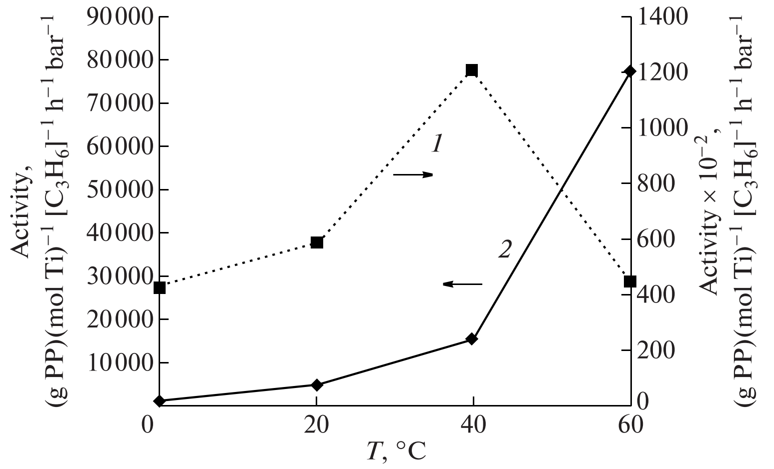


Fig. 3. Propene polymerization with **3**. Activators: (*1*) $B(C_6F_5)_3$ and (*2*) $[Ph_3C]^+[B(C_6H_5)_4]^-$.

active catalyst. The formation of these metallacycles should be favoured with increased temperature, and this effect can indeed be seen: increasing the temperature from 0 to 60°C decreases the activity significantly (entries *6–8*). However, the influence of the anion is apparent as well, the less coordinating $[B(C_6F_5)_4]^-$ seems to have an opposite effect: the activity increases with increasing temperature (entries *9–12*, and *17–20*).

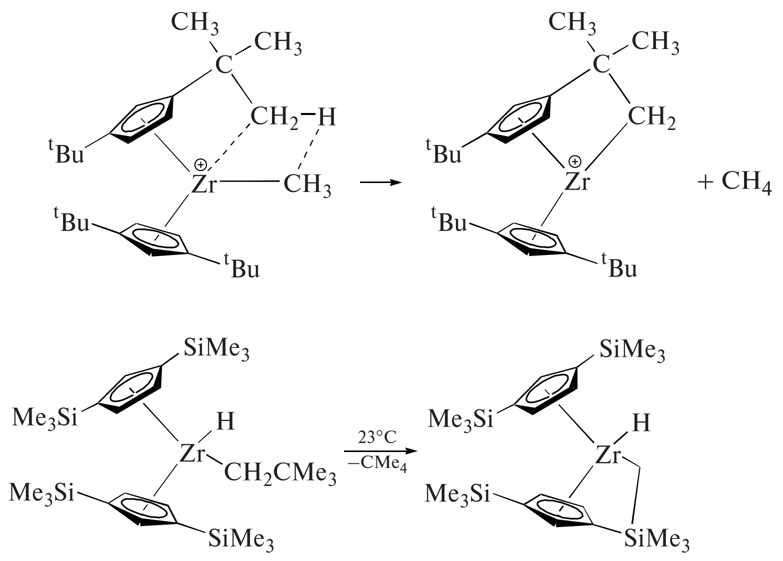
Table 3. Propene polymerization with compounds **1–3**

Entry no.	Compound,* μmol	Activator,** μmol	Temp., °C	Time, s	Yield, mg	Activity***	$M_w \times 10^{-3}$	M_w/M_n
1	**1** (20)	$B(C_6F_5)_3$ (20)	0	60	1891	25215	31.15	2.4
2	**1** (20)	$B(C_6F_5)_3$ (20)	20	60	101	18400	207.45	14.5
3	**1** (20)	$B(C_6F_5)_4$ (20)	0	150	952	50811	268	5.0
4	**1** (20)	$B(C_6F_5)_4$ (20)	20	90	626	75879	201.5	5.2
5	**2** (40)	$B(C_6F_5)_3$ (40)	0	1200	168.9	56300	125.5	5.2
6	**2** (40)	$B(C_6F_5)_3$ (40)	20	1200	144.2	65545	93.3	4.5
7	**2** (40)	$B(C_6F_5)_3$ (40)	40	1200	80.4	56355	64.2	3.7
8	**2** (40)	$B(C_6F_5)_3$ (40)	60	1200	8.4	14651	–	–
9	**2** (20)	$B(C_6F_5)_4$ (20)	0	324	563.9	13923	346.5	3.2
10	**2** (20)	$B(C_6F_5)_4$ (20)	20	300	532.3	19356	281.5	3.0
11	**2** (20)	$B(C_6F_5)_4$ (20)	40	300	744.2	42346	251.5	4.0
12	**2** (20)	$B(C_6F_5)_4$ (20)	60	480	930.2	81122	153	2.5
13	**3** (40)	$B(C_6F_5)_3$ (40)	0	72000	128.6	42800	99.4	8.9
14	**3** (40)	$B(C_6F_5)_3$ (40)	20	72000	172.3	58400	99.8	7.1
15	**3** (40)	$B(C_6F_5)_3$ (40)	40	72000	78.8	120700	–	–
16	**3** (40)	$B(C_6F_5)_3$ (40)	60	72000	25.6	44600	–	–
17	**3** (40)	$B(C_6F_5)_4$ (40)	0	97200	532.5	1314	297	7.8
18	**3** (40)	$B(C_6F_5)_4$ (40)	20	61200	941.7	5035	366.5	6.4
19	**3** (40)	$B(C_6F_5)_4$ (40)	40	25200	775.3	15526	194	3.7
20	**3** (40)	$B(C_6F_5)_4$ (40)	60	28800	1767.5	77071	98.3	2.8

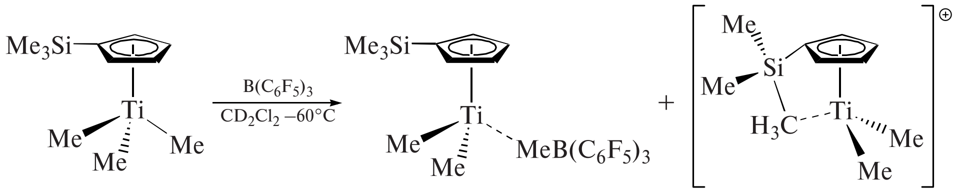
* Conditions: 1 bar propene pressure, 20 ml toluene, stirring rate 1000 rpm.

**$B(C_6F_5)_4 = [Ph_3C]^+[(B(C_6F_5)_4]^-$; $[Ph_3C]^+[(B(C_6F_5)_4]^-$ injected first, solvent removed under reduced pressure, 20 ml toluene added.

***In g PP/[(mol Ti) $[C_3H_6]$ h bar].



Scheme 1. Formation of a zirconacycle: Top: from reference [44], bottom: reference [45].



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Scheme 2. Proposed formation of a titanacyle.

The effect of the anion is well known and has been studied in detail, notably by Marks [46–51] and Bochmann [52]. Preliminary low temperature NMR studies of **2** indicate the presence of a second, outer sphere ion pair and are subject to a separate publication.

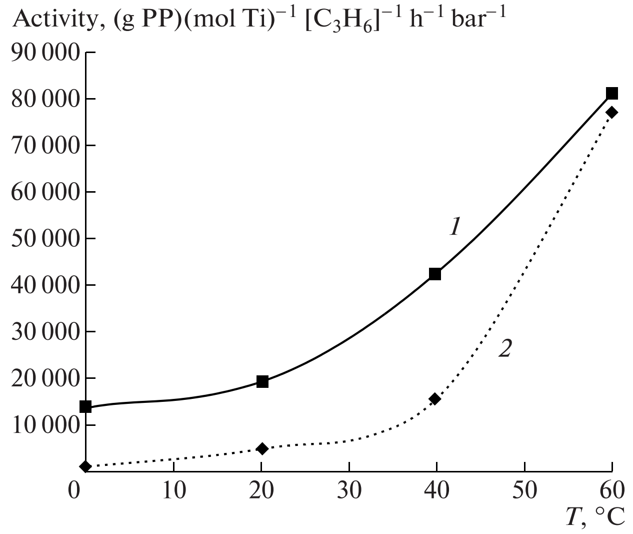

Fig. 4. Comparison between **2** (*1*) and **3** (*2*).

CONCLUSIONS

The trimethylsilyl substituted half-sandwich titanium compounds **1–3** show an unusual and interesting chemistry. Whereas propene polymerization with $[Ti(\eta^5\text{-}C_5Me_5)Me_3]$ when activated with $B(C_6F_5)_3$ yields a *quasi-living* catalyst for the formation of high molecular weight atactic polypropene, compounds **1–3** are by far less active. The formation of high molecular weight polypropene with narrow polydispersity could not be observed, but rather low molecular weight polypropene with broad polydispersity could be obtained. Obviously, this is due to the nature of the substituent on the cyclopentadienyl ring. The C_5Me_5 moiety is rather electron rich. The trimethylsilyl substituted cyclopentadienes are sterically more crowded than unsubstituted cyclopentadiene, but electronically comparable to it. Our original idea, to discriminate between steric and electronic effects which could lead to the *quasi-living* catalyst, were unfruitful due to the apparent side reactions the $-SiMe_3$ ligand is undergoing. We hoped the $-SiMe_3$ groups would be sterically similar to the C_5Me_5 moiety and thus the electronic effects could be separated from the steric ones. Unfortunately, due to the side reactions and the consequent formation of multiple catalytic sites this was not possible. Currently further investigations in the nature of the active species are undertaken and are subject to a further publication.

EXPERIMENTAL

General

All experiments were carried out under a nitrogen atmosphere by using standard Schlenk techniques. Solvents were dried over sodium (toluene, low in sulfur), sodium/potassium alloy (diethyl ether, light petroleum ether, bp 40–60°C), sodium/benzophenone (THF) and calcium hydride (dichloromethane). NMR solvents were dried over activated molecular sieves, freeze thawed and stored in Young's-Tap sealed ampoules.

NMR spectra were recorded on a Bruker DPX300 spectrometer and referenced to the residual solvent peak. Chemical shifts are quoted in ppm relative to tetramethylsilane. ^{13}C NMR were proton decoupled using a WALTZ sequence. CH-Coupling constants were measured by coupled INEPT. ^{13}C NMR of the polymer samples were recorded at 120°C in $C_2D_2Cl_4$ and proton decoupled using a WALTZ sequence. A pulse delay of 1 s was applied. On average 9000 scans were collected.

For X-ray structure analyses the crystals were mounted onto the tip of glass fibers, and data collection was performed with a BRUKER-AXS SMART APEX CCD diffractometer using graphite-monochromated MoK_α radiation (0.71073 Å). The data were reduced to F_0^2 and corrected for absorption effects with SAINT [53] and SADABS [54, 55], respectively. The structures were solved by direct methods and refined by full-matrix least-squares method (SHELXL97) [56]. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles. The diagram was drawn with 30% probability thermal ellipsoids and all hydrogen atoms were omitted for clarity. Crystallographic data (excluding structure factors) for the structure of compound **4** reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 665670 (**4**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internal.) +44-1223/336-033; e-mail: deposit@chemcrys.cam.ac.uk].

Preparation of $C_5H_5(SiMe_3)$

Sodiumhydride (40.0 g, 1 mol, 60% w/w in mineral oil) was washed with light petroleum, suspended in 900 ml THF and cooled to 0°C. Freshly distilled cyclopentadiene (66.10 g, 1 mol) was slowly added, the reaction mixture was stirred at 0°C for 30 min after complete addition. This reaction mixture was slowly added via a cannula to a mixture of 108.6 g (1 mol) trimethylchlorosilane in 500 ml THF and stirred for 1 h. After hydrolysis with water, the phases were separated and the aqueous phase extracted twice with 250 ml light petroleum. The combined organic phases were dried over $MgSO_4$, filtered, the solvent removed under reduced pressure. The crude yellow oil was distilled at atmospheric pressure yielding 28.2 g (204 mmol, 20%).

^{1}H NMR ($CDCl_3$, 300 MHz, 20°C): δ (ppm): 0.07 (s, 9H, $SiCH_3$); 3.48 (br, 1H, Cp); 6.59 (br, 2H, Cp); 6.69 (br, 2H, Cp).

Preparation of $C_5H_{6-x}(SiMe_3)_x$ ($x = 2, 3$)

Both ligands were prepared in a one-pot synthesis and later separated by distillation. Thus, sodiumhydride (80 g, 2 mol, 60% w/w in mineral oil) was washed with light petroleum and suspended in 1250 ml THF. Freshly distilled cyclopentadiene (66.10 g, 1 mol) was diluted with 250 ml THF and slowly added at 0°C. After complete addition the reaction mixture was stirred at ambient temperature for 30 min. Next the compound trimethylchlorosilane (252 ml, 2 mol) were carefully added at 0°C and stirred for 1 h. The reaction mixture was hydrolyzed with water and the phases were separated. The aqueous phase was extracted twice with 350 ml light petroleum. The combined organic phases were dried with $MgSO_4$ and the volatile removed under reduced pressure. The crude yellow oil was vacuum distilled using a 20 cm long Vigreux column yielding two products:

$C_5H_4(SiMe_3)_2$: bp (0.01 Torr) 36–44°C, 67 g, 318 mmol

^{1}H NMR ($CDCl_3$, 300 MHz, 20°C): δ (ppm): –0.05 (s, 18H, $SiCH_3$); 6.55 (m, 2H, Cp); 6.75 (m, 2H, Cp).

$C_5H_3(SiMe_3)_2$: bp (0.01 Torr) 44–58°C, 33 g, 116 mmol

^{1}H NMR ($CDCl_3$, 300 MHz, 20°C): δ (ppm): –0.05 (s, 18H, $SiCH_3$); 0.18 (s, 9H, $SiCH_3$); 6.52 (m, 1H, Cp); 6.67 (m, 1H, Cp); 6.78 (m, 1H, Cp).

*Preparation of [Ti(η^5-$C_5H_4SiMe_3$)Cl_3] (**1a**)*

The ligand $C_5H_5(SiMe_3)$ (4.14 g, 30 mmol) was treated with butyllithium (18.75 ml, 30 mmol, c = 1.6 mol/1) in 100 ml light petroleum. The white slurry was stirred for 30 min at ambient temperature and filtered. The white residue was washed with 100 ml light petroleum and suspended in 100 ml light petroleum. Neat $TiCl_4$ (3.3 ml, 30 mmol) was slowly added via syringe. The yellow-green reaction mixture was stirred for 1 h at ambient temperature. The reddish filtrate was concentrated and cooled to –40°C yielding: 4.16 g (14.3 mmol, 48%) of the desired compound as a yellow solid. (Found: C 33.3%, H 4.6%, Cl 36.3%; $C_8H_{13}Cl_3SiTi$ requires: C 33.0%, H 4.5%, Cl 36.5%).

^{1}H NMR ($CDCl_3$, 300 MHz, 20°C): δ (ppm): 0.42 (s, 9H, $SiCH_3$); 7.12 (“t”2H, Cp); 7.32 (“t”, 2H, Cp).

^{13}C NMR ($CDCl_3$, 75.5 MHz, 20°C): δ (ppm): 0.8 ($SiCH_3$); 126.5 (Cp); 129.5 (Cp); 142.3 (*i*-C–Cp).

Preparation of $[Ti(\eta^5\text{-}C_5H_3(SiMe_3)_2)Cl_3]$ *(**2a**)*

The compound $[Ti(\eta^5\text{-}C_5H_3(SiMe_3)_2)Cl_3]$ was prepared following a literature procedure [57, 58]. Yield: 7.94 g (21.8 mmol, 70.7%).

Preparation of $[Ti(\eta^5\text{-}C_5H_2(SiMe_3)_3)Cl_3]$ *(**3a**)*

The compound $[Ti(\eta^5\text{-}C_5H_2(SiMe_3)_3)Cl_3]$ was prepared following a literature procedure [59]. Yield: 4.74 g (10.9 mmol, 26%).

Preparation of $[Ti(\eta^5\text{-}C_5H_{5-x}(SiMe_3)_x)Cl_3]$ $(x = 1–3)$

General procedure: The trichlorides (**1a**), (**2a**), or (**3a**) were dissolved in 180 ml diethylether and cooled to –79°C. Three equivalent of the compound methylmagnesiumchloride ($c = 3$ mol/l in diethylether) were slowly added, the reaction mixture was slowly warmed to 0°C. The volatiles of the grey slurry were removed under reduced pressure, the residue extracted with light petroleum at 0°C. The volatiles of the extract were removed under reduced pressure.

$(Ti(\eta^5\text{-}C_5H_4SiMe_3)Me_3$ (**1**) Yield: 1.6 g, 6.9 mmol, 50.1% (yellow oil).

(Found: C 54.85%, H 9.35%; $C_{11}H_{23}SiTi$ requires: C 57.13%, H 10.02%, low C due to formation of SiC.)

^{1}H NMR ($CDCl_3$, 300 MHz, 20°C): δ (ppm): 0.25 (s, 9H, $SiCH_3$); 1.16 (s, 9H, $TiCH_3$); 6.47 (br, 4H, Cp).

^{13}C NMR ($CDCl_3$, 75.5 MHz, 20°C): δ (ppm): –0.4 ($SiCH_3$); 62.6 ($TiCH_3$); 117.2 (Cp); 127.2 (*i*-C–Cp).

$Ti(\eta^5\text{-}C_5H_3(SiMe_3)_2)Me_3$ (**2**) Yield: 2.63 g, 8.7 mmol, 90.5% (yellow microcystalline solid).

(Found: C 55.89%, H 9.48%; $C_{14}H_{30}Si_2Ti$ requires: C 55.60%, H 10.00%.)

^{1}H NMR (CD_2Cl_2, 300 MHz, 20°C): δ (ppm): 0.17 (s, 18H, $SiCH_3$); 1.09 (s, 9H, $TiCH_3$); 6.55 (s, 3H, Cp).

^{13}C NMR (CD_2Cl_2, 75.5 MHz, 20°C): δ (ppm): –0.2 ($SiCH_3$); 62.8 ($TiCH_3$); 121.6 (Cp), 122.6 (Cp); 132.8 (*i*-C–Cp).

$Ti(\eta^5\text{-}C_5H_2(SiMe_3)_3)Me_3$ (**3**) Yield: 3.1 g, 8.3 mmol, 76% (dark solid).

(Found: C 53.84%, H 9.98%; $C_{17}H_{38}Si_3Ti$ requires: C 54.49%, H 10.22%.)

^{1}H NMR (C_6D_6, 300 MHz, 20ºC): δ (ppm): 0.36 (s, 9H, $SiCH_3$); 0.47 (s, 18H, $SiCH_3$); 1.66 (s, 9H, $TiCH_3$); 7.12 (s, 2H, Cp).

^{13}C NMR (C_6D_6, 75.5 MHz, 20°C): δ (ppm): 0.4 ($SiCH_3$); 1.2 ($SiCH_3$); 64.3 ($TiCH_3$); 130.4 (Cp); 134.8 (*i*-C–Cp).

Preparation of $[\{Ti(\eta^5\text{-}C_5H_3(SiMe_3)Cl_2)\}O]$ *(**4**)*

300 mg of the trichloride **1a** were dissolved in wet pentane and the solution was covered with a piece of filter paper. The solvent was slowly evaporated over the course of 2 weeks to yield small, yellow needles suitable for X-ray crystallography. Yield: 380.4 mg, 0.7 mmol 70%.

(Found: C 36.00%, H 4.70%; $C_{16}H_{26}Cl_4OSi_2Ti_2$ requires: C 36.39%, H 4.96%.)

^{1}H NMR ($CDCl_3$, 500 MHz, 20°C): δ (ppm): 0.35 (s, 9H, $SiCH_3$); 0.34 (s, 9H, $SiCH_3$); 6.69 (“t,” 2H, Cp), 6.80 (“t,” 2H, Cp), 6.93 (“t”, 2H, Cp), 7.12 (“t,” 2H, Cp).

^{13}C NMR ($CDCl_3$, 125 MHz, 20ºC): δ (ppm): –0.6 ($SiCH_3$), –0.4 ($SiCH_3$), 121.9 (Cp), 125.1 (Cp). 126.2 (Cp), 128.6 (Cp), 132.7 (*i*-C–Cp), 138.9 (*i*-C–Cp).

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