Synthesis and reactivity of a tethered diene cyclopentadiene, $(C_5Me_4H)SiMe_2(CH_2CH=CHCH=CH_2)$, and its alkali metal salts

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Abstract

$(C_5Me_4H)SiMe_2Cl$ reacts with $(THF)KCH_2CH=CHCH=CH_2$ to form $(C_5Me_4H)SiMe_2(CH_2CH=CHCH=CH_2)$ (**1**). Compound **1** reacts with KH and n-BuLi to make $M(C_5Me_4)SiMe_2(CH_2CH=CHCH=CH_2)$, M = K, **2**; Li, **3**, respectively. Carbon–silicon cleavage occurs when **1** reacts with K to form $(C_5Me_4H)K$, which crystallizes from dimethoxyethane as $[(C_5Me_4H)K(DME)]_x$. This potassium salt has an extended structure which generates bent metallocene $(C_5Me_4H)_2K(DME)$ sub-structures which have 133.9° ring centroid–K–ring centroid angles. Compound **1** reacts with $TiCl_4$ to make $(C_5Me_4H)TiCl_3$ (**5**), which has a piano stool structure.

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1. Introduction

Cyclopentadienyl ligands to which other donor functionalities are attached have provided a useful means to enhance the binding ability of this common ligand [1–15]. A variety of ligands have been tethered to cyclopentadienyl rings including amines, ethers, and cyclopentadienyl groups as in the ansa metallocenes. Attachment of functionality to cyclopentadienyl ligands can also be used to investigate the chemistry of the functional group, since the group is held in close proximity to the metal and the cyclopentadienyl ligand provides a well-defined coordination geometry in the complex. Olefin chemistry has been studied in this way by tethering allyl groups to cyclopentadienides [8,9,12] as well as to other ligands [10,11]. Although this approach has been used with olefins, to our knowledge it has not been utilized with dienes.

Tethered diene systems are of interest for studies of the highly efficient lanthanide-based polymerization of dienes to high *cis*-1,4-polydienes [16–18] in a well-defined coordination geometry. We report here the first synthesis of a diene-substituted cyclopentadienyl system, its conversion to alkali metal salts, and some preliminary reaction chemistry.

2. Experimental

The chemistry described below was performed under nitrogen with rigorous exclusion of air and water by using Schlenk, vacuum line, and glovebox techniques. Solvents were saturated with UHP grade Ar and dried by passage through drying columns by GlassContour® (Irvine, CA). Benzene-d_6 was distilled over NaK alloy and benzophenone. $CH_2=CHCH_2CH=CH_2$, KH, and n-BuLi (1.0 M in hexane) were purchased from Aldrich. $CH_2=CHCH_2CH=CH_2$ was distilled under nitrogen at 50 °C before being used. KH was washed with hexane before use. $(C_5Me_4H)Me_2SiCl$ [19], and $(THF)K(CH_2CH=CHCH=CH_2)$ [20] were prepared as described in the literature. $(THF)K(CH_2CH=CHCH=CH_2)$ was crystallized from THF at −35 °C before use. ^{1}H- and ^{13}C-NMR spectra were obtained using an Omega 500 MHz and a GN 500 MHz NMR spectrometers. IR spectra were obtained using an ASI ReactIR 1000

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spectrometer. GCMS spectra were obtained using a 2000 Series Thermo Finnigan Trace Mass Spectrometer.

2.1. Synthesis of $(C_5Me_4H)SiMe_2(CH_2CH=CHCH=CH_2)$ (1)

In a 500 ml Schlenk flask, freshly distilled $(C_5Me_4H)Me_2SiCl$ (2.98 g, 13.9 mmol) was added to 200 ml of THF and cooled to $-78\ ^\circ$C. A 50 ml THF solution of $(THF)K(CH_2CH=CHCH=CH_2)$ (3.00 g, 16.8 mmol) was added slowly via cannula. After the $(THF)K(CH_2CH=CHCH=CH_2)$ was added, the mixture was allowed to warm to room temperature (r.t.) and was stirred overnight. THF was removed under vacuum and water (50 ml) was added to quench the solution. The mixture was transferred to a separatory funnel and diluted with 100 ml of Et_2O. The organic layer was separated and washed with a saturated NH_4Cl solution (230 ml) and then a saturated NaCl solution (230 ml). The combined ether solutions were dried over $MgSO_4$ and concentrated to give a light yellow liquid of **1** (2.46 g, 72%) at 90% purity by GCMS. To further purify **1**, column chromatography using silica gel (3:2 hexanes–Et_2O with 1.5% Et_3N) was used to give a pure light yellow liquid of **1** (2.16 g, 88%). ^{1}H-NMR (C_6D_6, 25 C) δ 6.64 (m, 1H, C*H*CH$_2$), 6.03 (t, 1H, CHC*H*CH), 5.42 (q, 1H, CH$_2$C*H*CH), 5.16 (d, 1H, CHC*H*$_2$) 5.04 (d, 1H, CHC*H*$_2$), 2.72 (s, 1H, CC*H*SiMe$_2$), 1.90 (s, 6H, C$_5$(C*H*$_3$)$_4$), 1.80 (s, 6H, C$_5$(C*H*$_3$)$_4$), 1.57 (d, 2H, SiMe$_3$C*H*$_2$), 0.01 (s, 6H, Si(C*H*)$_2$). ^{13}C-NMR (C_6D_6, 25 C) δ 138.0 (*C*$_5$Me$_5$), 137.6 (*C*$_5$Me$_5$), 135.9 (CH*C*HCH$_2$), 132.8 (CH$_2$*C*HCH), 129.2 (CH*C*HCH), 113.0 (*C*SiMe$_2$), 112.4 (*C*SiMe$_2$), 115.7 (CH*C*H$_2$), 17.0 (Me$_2$Si*C*H$_2$) 14.3 (C$_5$*Me*$_5$), 11.4 (C$_5$*Me*$_5$), -3.31 (Si*Me*$_2$). IR (thin film) 3084 w, 3007 w, 2964 m, 2914 m, 2860 m, 2737 w, 1791 w, 1733 w, 1637 m, 1686 w, 1552 w, 1436 m, 1301 w, 1251 s, 1220 m, 1143 m, 1046 m, 992 s, 953 m, 896 m, 838 m, 703 w, 652 w, 567 w cm^{-1}.

2.2. Synthesis of $K(C_5Me_4)SiMe_2(CH_2CH=CHCH=CH_2)$ (2)

In a nitrogen-containing glovebox, solid KH (0.072 g, 1.8 mmol) was added slowly to a light yellow solution of **1** (0.47 g, 1.9 mmol) in 10 ml of THF. The reaction was stirred overnight during which time the solution turned dark yellow and gas evolved. THF was removed under vacuum and the solids were washed with hexane (35 ml) and dried under vacuum to yield **2** as a white solid (66 mg, 79%). ^{1}H-NMR (d-THF, 25 C) δ 6.30 (m, 1H, C*H*CH$_2$), 5.91 (t, 1H, CHC*H*CH), 5.77 (q, 1H, CH$_2$C*H*CH), 4.94 (d, 1H, CHC*H*$_2$) 4.77 (d, 1H, CHC*H*$_2$), 2.04 (s, 6 H, C$_5$(C*H*$_3$)$_4$), 1.89 (s, 6 H, C$_5$(C*H*$_3$)$_4$), 1.66 (d, 2H, SiMe$_3$C*H*$_2$), 0.12 (s, 6H, Si(C*H*)$_2$). ^{13}C-NMR (d-THF, 25 C) δ 139.3 (*C*$_5$Me$_5$),

135.7 (*C*$_5$Me$_5$), 129.9 (CH*C*HCH$_2$), 118.1 (CH$_2$*C*HCH), 113.2 (CH*C*HCH), 111.7 (CH*C*H$_2$), 100.4 (*C*SiMe$_2$), 27.5 (Me$_2$Si*C*H$_2$) 14.8 (C$_5$*Me*$_5$), 11.7 (C$_5$*Me*$_5$), 1.25 (Si*Me*$_2$).). IR (thin film) 3084 w, 3007 w, 2922 m, 2856 m, 2729 w, 2420 m, 2351 w, 1934 s, 1668 w, 1637 w, 1552 w, 1436 w, 1405 w, 1378 m, 1301 w, 1251 s, 1220 m, 1181 w, 1143 m, 1112 w, 1046 m, 992 s, 953 m, 896 m, 838 m, 799 w, 699 m, 517 s cm^{-1}.

2.3. Synthesis of $Li(C_5Me_4)SiMe_2(CH_2CH=CHCH=CH_2)$ (3)

In a 100 ml Schlenk flask **1** (0.25 g, 1.0 mmol) in 50 ml of hexane was cooled to $-78\ ^\circ$C and *n*-BuLi (0.90 ml, 0.90 mmol) was added slowly via syringe. The reaction was stirred at $-78\ ^\circ$C for 2 h and then at r.t. overnight. The hexane was removed under vacuum and the solids were taken into a nitrogen-containing glovebox. The yellow solids were washed with hexane (320 ml) to yield a beige powder (0.21 g, 83%). ^{1}H NMR (d-THF, 25 C) δ 7.17 (m, 1H, C*H*CH$_2$), 6.24 (t, 1H, CHC*H*CH), 5.82 (q, 1H, CH$_2$C*H*CH), 4.84 (d, 1H, CHC*H*$_2$) 4.70 (d, 1H, CHC*H*$_2$), 2.03 (s, 6H, C$_5$(C*H*$_3$)$_4$), 1.90 (s, 6H, C$_5$(C*H*$_3$)$_4$), 1.29 (d, 2H, SiMe$_3$C*H*$_2$), 0.17 (s, 6H, Si(C*H*$_3$)$_2$). IR (thin film) 3084 w, 3007 w, 2922 m, 2856 m, 2729 w, 2420 m, 2351 w, 1934 s, 1668 w, 1637 w, 1552 w, 1436 w, 1405 w, 1378 m, 1301 w, 1251 s, 1220 m, 1181 w, 1143 m, 1112 w, 1046 m, 992 s, 953 m, 896 m, 838 m, 799 w, 699 m, 517 s cm^{-1}.

2.4. $[(C_5Me_4H)K(DME)]_x$ (4)

Potassium metal (0.026 g, 0.66 mmol) was added to a solution of **1** (0.18 g, 0.73 mmol) in 10 ml of THF. The mixture was stirred overnight and the THF was removed under vacuum. The beige powder was washed with hexane to yield an off-white solid. The solid was dissolved in 5 ml of DME and colorless crystals of **4** (0.077 g, 42%) formed after 2 days at room temperature which were identified by X-ray crystallography.
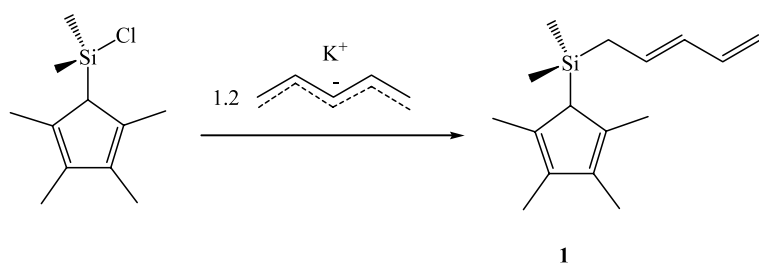
2.5. $(C_5Me_4H)TiCl_3$ (5)

A slightly yellow solution of **1** (0.13 g, 0.51 mmol) in 2 ml of toluene was added dropwise to a yellow solution of TiCl$_4$ (0.10 g, 0.51 mmol) in 8 ml of toluene. The reaction was stirred overnight at which time the color had changed to dark red. The mixture was centrifuged to remove some thick insoluble materials. The toluene was removed under vacuum and the red solids were dissolved in a 4:1 toluene–hexane solution. The solution was kept at $-35\ ^\circ$C overnight at which time large red crystals of **5** formed (0.074 g, 51%) which were identified by X-ray crystallography. ^{1}H-NMR (C_6D_6, 25 C) δ 1.920 (s, 3H, CH$_3$), 1.916 (s, 3H, CH$_3$), 1.820 (s, 3H, CH$_3$), 1.815 (s, 3H, CH$_3$).

2.6. X-ray data collection, structure solution and refinement for 4 and 5

2.6.1. [(C5Me4H)K(DME)]x (4)

A colorless crystal of approximate dimensions 0.18 × 0.21 × 80 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART [21] program package was used to determine the unit-cell parameters and for data collection (30 s/ frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT [22] and SADABS [23] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL [24] program. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/c$ which was later determined to be correct. The polymeric structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors [25] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. At convergence, $wR_2 = 0.1358$ and Goof = 1.051 for 154 variables refined against 3716 data. As a comparison for refinement on F, $R_1 = 0.0459$ for those 2963 data with $I > 2.0\sigma(I)$.

Table 1
X-ray data collection parameters [a] for [(C5Me4H)K(DME)]x (4) and (C5Me4H)TiCl3 (5)

	[C13H23KO2]∞ (4)	C9H13Cl3Ti (5)
Empirical formula	[C$_{13}$H$_{23}$KO$_2$]$_\infty$ (4)	C$_9$H$_{13}$Cl$_3$Ti (5)
Formula weight	250.41	275.44
Temperature (K)	163(2)	185(2)
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pnma$
a (Å)	8.7091(5)	12.0387(6)
b (Å)	18.5437(11)	13.7913(7)
c (Å)	10.1796(6)	7.1519(4)
α (°)	90	90
β (°)	110.5730(10)	90
γ (°)	90	90
V (Å^3)	1539.15(16)	1187.43(11)
Z	4	4
ρ_{calcd} (Mg m^{-3})	1.081	1.541
μ (mm^{-1})	0.332	1.349
R_1 [b] (all data)	0.0598	0.0300
wR_2 [c] (all data)	0.01358	0.0799

[a] Radiation: Mo–K$_\alpha$ ($\mu = 0.71073$ Å). Monochromator: highly oriented graphite.
[b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[c] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]]^{1/2}$.

3. Results and discussion

3.1. Synthesis

(1)

1

2.6.2. (C5Me4H)TiCl3 (5)

A red crystal of approximate dimensions 0.16 × 0.21 × 0.37 mm was handled as described for 4. The diffraction symmetry was mmm and the systematic absences (Table 1) were consistent with the orthorhombic space group $Pnma$ which was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The molecule was located on a mirror plane. Hydrogen atoms were included using a riding model. At convergence, $wR_2 = 0.0799$ and GOF = 1.112 for 65 variables refined against 1521 data. As a comparison for refinement on F, $R_1 = 0.0277$ for those 1407 data with $I > 2.0\sigma(I)$.

Olefin tethered cyclopentadienes are typically synthesized by addition of allyl Grignard reagents to cyclopentadienyl dimethyl silyl chlorides [26,27]. The diene-substituted tetramethylcyclopentadiene, (C5Me4H)-SiMe2(CH2CH=CHCH=CH2) (1) can also be synthesized in this way from (C5Me4H)SiMe2Cl [19] and the pentadienyl magnesium chloride [20], but the purity of the product was poor. A better synthesis, shown in Eq. (1), uses (C5Me4H)SiMe2Cl and (THF)KCH2CH=CHCH=CH2, which can be readily prepared from 1,4-pentadiene and potassium metal in the presence of an excess amount of triethyl amine [28]. Complex 1 is very sensitive to acidic conditions and can decompose to C5Me4H. Complex 1 can be purified by column

(2)
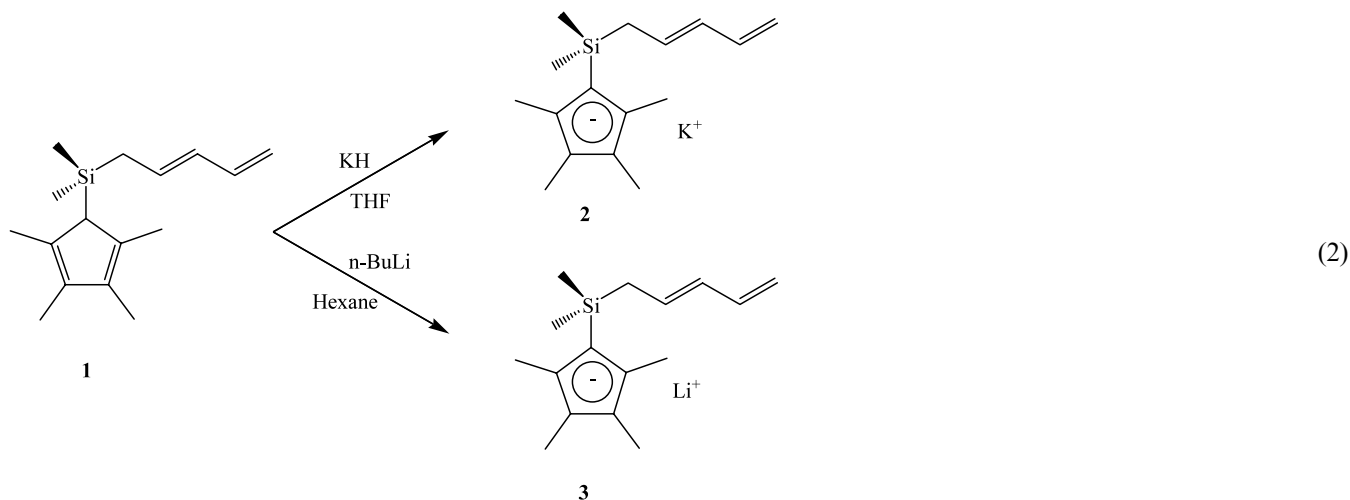
chromatography using a silica gel column washed with a 1.5% solution of triethyl amine to remove any acidic residues. The *cis* and *trans* isomers of **1** are observed by ^{1}H-NMR spectroscopy and by GCMS. The ^{1}H-NMR spectrum in C_6D_6 shows two peaks for C_5Me_4 at 1.89 and 1.80 ppm and two for $SiMe_2$ at -0.02 and -0.04 ppm. The diene protons also display two sets of resonances.
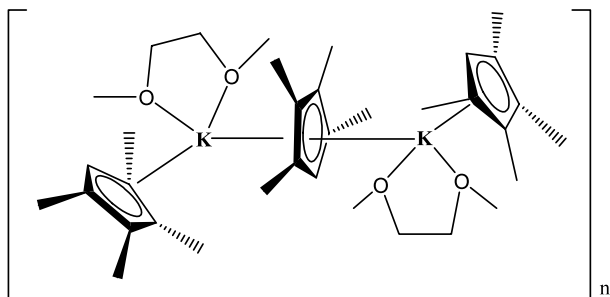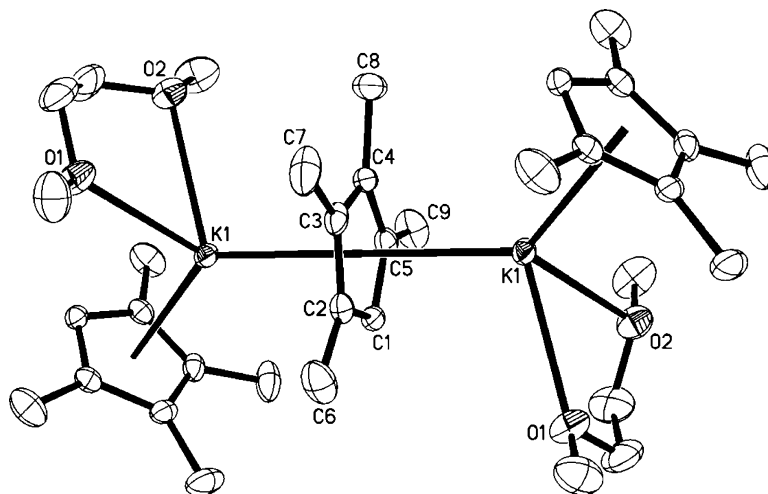
Complex **1** reacts with KH and *n*-BuLi to form $M[(C_5Me_4)SiMe_2(CH_2CH{=}CHCH{=}CH_2)]$, M = K, **2**; Li, **3**, respectively (Eq. (2)). The reaction of potassium metal with **1** did not form **2**. Instead, **1** reacts with potassium metal in the presence of DME to form the decomposition product $[(C_5Me_4H)K(DME)]_x$ (**4**) Fig. 1Thermal ellipsoid plot of $[(C_5Me_4H)K(DME)]_n$ (**4**) drawn at the 50% probability level. (Eq. (3)), which was identified by X-ray crystallography as described below. Cleavage of carbon silicon bonds with Na–K has previously been reported with silyl carbinols of general formula $R_3SiC(OH)R_2$ [29].

Carbon–silicon cleavage is also observed when **1** reacts with $TiCl_4$. $(C_5Me_4H)TiCl_3$ (**5**) was isolated from this reaction and characterized by X-ray crystallography (Eq. (4)). $[C_5Me_4P(^tBu)(NEt_2)]TiCl_3$ was previously made in a similar way from $Me_3SnC_5Me_4P(^tBu)(NEt_2)$ and $TiCl_4$ [30].

4

(3)

Fig. 1. Thermal ellipsoid plot of $[(C_5Me_4H)K(DME)]_n$ (**4**) drawn at the 50% probability level.

Table 2
Selected bond distances (Å) and angles (°) for $[(C_5Me_4H)K(DME)]_x$ (**4**)

Bond	**4**	Angle	**4**
K(1)–O(1)	2.774(2)	O(1)–K(1)–Cnt	105.2
K(1)–O(2)	2.797(2)	O(2)–K(1)–Cnt	113.3
K(1)–C(1)	3.043(2)	O(1)–K(1)–Cnt′1	115.5
K(1)–C(2)	2.997(2)	O(2)–K(1)–Cnt′1	105.1
K(1)–C(3)	2.970(2)	Cnt–K(1)–Cnt′1	133.9
K(1)–C(4)	3.007(2)	K(1)–Cnt′1–K(1)′2	178.4
K(1)–C(5)	3.064(2)		
K(1)–C(1)′1	2.989(2)		
K(1)–C(2)′1	3.014(2)		
K(1)–C(3)′1	3.028(2)		
K(1)–C(4)′1	3.027(2)		
K(1)–C(5)′1	2.997(2)		
K(1)–Cnt	2.769		
K(1)–Cnt′1	2.763		

Cnt is the ring centroid for C(1)–C(5), Cnt1′ is the ring centroid for C(11)–C(15).

$$TiCl_4 + \mathbf{1} \xrightarrow{\text{toluene}} \mathbf{5} \tag{4}$$
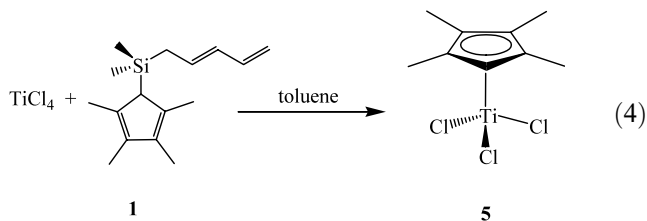
3.2. Structural studies

3.2.1. $[(DME)K(\mu\text{-}C_5Me_4H)]_n$ (**4**)

Complex **4** crystallizes with the extended structure shown in Fig. 1 (Table 2) which generates a bent metallocene coordination environment around potassium [31]. Table 3 compares **4** with the closest structurally related $[L_2K(C_5Me_5)_2]_n$ species whose extended structures form metallocene sub-units, $[(pyridine)_2K(C_5Me_5)]_n$, (**6**) [32], and $[(THF)_2K(\mu\text{-}C_5Me_5)]_n$, (**7**) [33]. The 178.4° K–(ring centroid)–K-angle of **4** is similar to the analogous near-linear angles in the C_5Me_5 structures. The C_5Me_4H rings are oriented within the bent metallocene $[(C_5Me_4H)_2K]^-$ subunit such that the hydrogen-substituted carbon atoms are trans to each other, i.e.
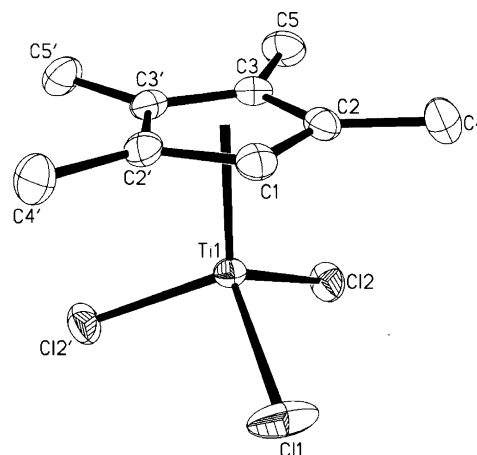

Fig. 2. Thermal ellipsoid plot of $(C_5Me_4H)TiCl_3$ (**5**) drawn at the 50% probability level.

one H is toward the back of the bent sandwich and one is toward the front. The methyl groups of adjacent rings are staggered with respect to each other. This arrangement allows a slightly smaller (ring centroid)–K–(ring centroid) angle in **4** compared to the C_5Me_5 structures. The K–(ring centroid) and K–$C(C_5Me_4)$ average distances in **4** are also slightly smaller than those in the C_5Me_5 structures. The 2.989(2) and 3.043(2) Å K–$C(C_5Me_4H)$ distances for the unique carbon with hydrogen rather than methyl as a substituent are in the middle of the 2.970(2)–3.064(2) Å range of K–$C(C_5Me_4H)$ distances in **4**. The K–O(DME) distances are similar to the K–O(THF) distance in $[(C_5Me_5)K(THF)_2]_n$ (Table 2).

Table 4
Selected bond distances (Å) and angles (°) for $(C_5Me_4H)TiCl_3$ (**5**)

Bond	**2**	Angle	**2**
Ti(1)–Cl(1)	2.2394(8)	Cnt–Ti(1)–Cl(1)	118.2
Ti(1)–Cl(2)	2.2444(5)	Cnt–Ti(1)–Cl(2)	114.0
Ti(1)–Cl(2)#1	2.2444(5)	Cl(1)–Ti(1)–Cl(2)	102.77(2)
Ti(1)–C(1)	2.306(2)	Cl(1)–Ti(1)–Cl(2)#1	102.77(2)
Ti(1)–C(2)	2.3386(17)	Cl(2)–Ti(1)–Cl(2)#1	103.24(3)
Ti(1)–C(3)	2.3828(17)		
Ti(1)–Cnt	2.014		

Table 3
Selected bond distances (Å) and angles (°) for $[(C_5Me_4H)K(DME)]_n$ (**4**), $[(THF)_2K(\mu\text{-}C_5Me_5)]_n$ (**6**), and $[(pyridine)_2K(\mu\text{-}C_5Me_5)]_n$ (**7**), arranged according to decreasing (ring centroid)–K–(ring centroid) angle

Compound	K–Cent–K (°)	Cent–K–Cent (°)	K–Cent (Å)	K–C avg (Å)	K–O (Å)	K–N (Å)	Reference
7	172.4	138	2.79	3.03	–	2.879(2) 2.974(2)	[12]
6	179.0	137.9	2.821	3.059(8)	2.807(4)	–	[13]
4	178.4	133.9	2.769	3.011(18)	2.774(2) 2.797(2)		This work

3.2.2. $(C_5Me_4H)TiCl_3$ (5)

The coordination geometry of the titanium atom in **5** can be described as a piano-stool configuration typical for half sandwich complexes (Fig. 2), e.g. $(C_5H_5)TiCl_3$ [34], $[C_5Me_4P(^tBu)(NEt_2)]TiCl_3$ [30], and $(C_5Me_4\text{-}CH_2CH_2Ph)TiCl_3$ [35] (Table 4). The three independent Ti–C bond lengths are 2.306(2), 2.3386(17), and 2.3828(17) Å with the shortest Ti–C distances involving the hydrogen-substituted carbon atom. The 2.2394(8)–2.2444(5) Å Ti–Cl distances as well as the 102.77° (2) and 103.24°(3) Cl–Ti–Cl and the 114.0° and 118.2° cnt–Ti–Cl angles have values similar to those of other related cyclopentadienyl titanium trichloride complexes [30,34–38].

4. Conclusion

A diene functionality can be tethered to tetramethyl-cyclopentadiene and the corresponding potassium and lithium cyclopentadienyls prepared. This cyclopentadienyl system readily undergoes Si–C cleavage with acid, potassium, and $TiCl_4$. It must be handled with care when it is attached to other metals.

5. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 214507 and 214508 for compounds $[(DME)K(\mu\text{-}C_5Me_4H)]_n$ (**4**) and $(C_5Me_4H)TiCl_3$ (**5**). 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).

Acknowledgements

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