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FULL PAPER

ansa-Metallocenes with a Ph_2Si bridge: molecular structures of $HfCl_2[Ph_2Si(\eta^5-C_{13}H_8)(\eta^5-C_5H_4)]$ and $HfCl_2[Ph_2Si(C_{13}H_9)(\eta^5-C_5H_4)]_2$ †

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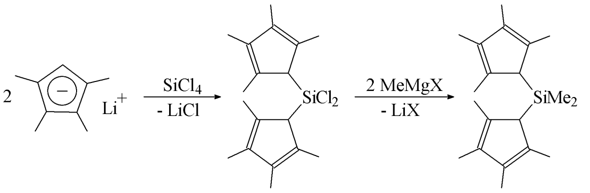
A mixture of *rac*- and *meso*-$HfCl_2[Ph_2Si(\eta^5-C_9H_6)_2]$ was synthesized by treatment of $HfCl_4$ with the dilithium salt of di(1*H*-inden-1-yl)diphenylsilane. These complexes were isolated after fractional crystallization in 15.5 and 8.5% yields, respectively. A sterically strained *ansa* complex $HfCl_2[Ph_2Si(\eta^5-C_{13}H_8)(\eta^5-C_5H_4)]$ was synthesized in 62% yield by treatment of $HfCl_4$ with the dilithium salt of cyclopentadienyl(fluoren-9-yl)diphenylsilane. Both this compound, and the by-product of reaction, $HfCl_2[Ph_2Si(C_{13}H_9)(\eta^5-C_5H_4)]_2$, were characterized by crystal structure analysis.

1 Introduction

The stereorigid *ansa*-metallocenes are known to be promising homogeneous catalyst precursors for stereoselective propene polymerization.[1,2] The *ansa* complexes, particularly fluorenyl-cyclopentadienyl compounds bridged with the bulky CPh_2 group were recently found to have unprecedented catalytic performance in olefin polymerization.[3,4] Similar complexes with a bulky Ph_2Si bridge are poorly studied,[5,6] mostly because of the more difficult preparation. Whereas bis-cyclopentadienyl ligands with a CPh_2 bridge are readily available *via* nucleophilic addition of cyclopentadienyllithium to diphenylfulvene, ligands with a Ph_2Si bridge can be prepared only *via* nucleophilic substitution at silicon. If nucleophilic substitution at a sterically hindered silicon center, *e.g.* in $Ph_2(Cp')SiCl$, is slow, attack of an organolithium or analogous reagent at such a chlorocyclopentadienylsilane is accompanied by transmetallation leading to decreased yields of the target ligand. In this case, an improvement of yield can be achieved either by optimization of reaction conditions or by using an alternative approach, which has been described *e.g.* for the synthesis of $Me_2Si(C_5Me_4H)_2$ (eqn. 1).[7]



(1)

This work is aimed at the synthesis and characterization of hafnium complexes containing bulky $Ph_2Si(\eta^5-C_{13}H_8)(\eta^5-C_5H_4)$ and $Ph_2Si(\eta^5-C_9H_6)_2$ ligands ($C_{13}H_8$ = fluorenyl, C_9H_6 = indenyl). The sterically strained unbridged metallocene $HfCl_2[Ph_2Si(C_{13}H_9)(\eta^5-C_5H_4)]_2$ has also been characterized. These hafnium complexes can be considered as the precursors of efficient polymerization catalysts.

2 Results and discussion

Synthesis and NMR study of ligands and metal complexes

Di(1*H*-inden-1-yl)diphenylsilane was synthesized by treatment of Ph_2SiCl_2 with 2 equivalents of indenyllithium (eqn. 2). The desired product was isolated in 21% yield after recrystallization from cold pentane. This product turned out to be a *ca.* 50 to 50 mixture of isomeric *rac* and *meso* compounds. The ^1H NMR spectrum (in $CDCl_3$) includes characteristic broad triplets at δ 4.369 ($J = 1.9$) and 4.414 ($J = 1.8$ Hz) attributed to allylic protons H(1) of indenyl fragments. Resonances at δ 6.690 (dd, $J = 1.9$, $J = 14.2$ Hz) and 6.680 ($J = 1.7$, $J = 14.3$ Hz) can be attributed to H(2), and multiplets at δ 6.765 and 6.745 are likely to belong to H(3).

The low yield of the product is accounted for by a metallation side reaction (*e.g.*, eqn. 3; pathway **a**), which can be faster (particularly in the case of organolithium reagents) than the nucleophilic substitution at the sterically hindered silicon center (eqn. 3; pathway **b**).

An attempt to purify the compound using high vacuum sublimation failed. At 120 °C we observed the rearrangement of isomeric di(1*H*-inden-1-yl)diphenylsilanes into the more thermodynamically stable isomer. From the evidence of NMR spectra, this isomer contains two equivalent indenyl fragments with silicon at the vinyl position of the indenyl system. This sigmatropic shift equilibrium sets in within several minutes. So, the resulting mixture contains up to 70% of this vinylic isomer, *ca.* 5% of the isomer with both vinylindenyl and 1*H*-inden-1-yl fragments, and *ca.* 25% of a *rac*/*meso* mixture of di(1*H*-inden-1-yl)diphenylsilanes. The recrystallization of this mixture from cold MeOH gave the desired symmetrical vinylic isomer with *ca.* 90% purity.

It is well known that more electronegative substituents at Si in cyclopentadienylsilanes should stabilize vinylsilyl isomers

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† Electronic supplementary information (ESI) available: characterization data for silanes and compounds **1**–**3**. See http://www.rsc.org/suppdata/dt/b0/b009280k/

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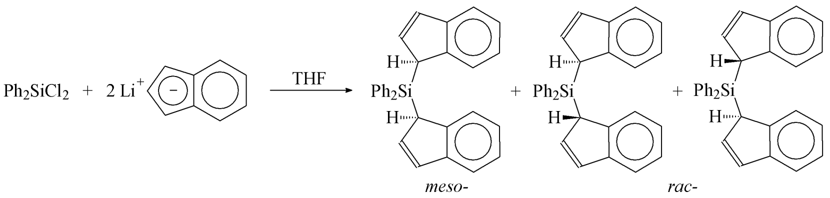

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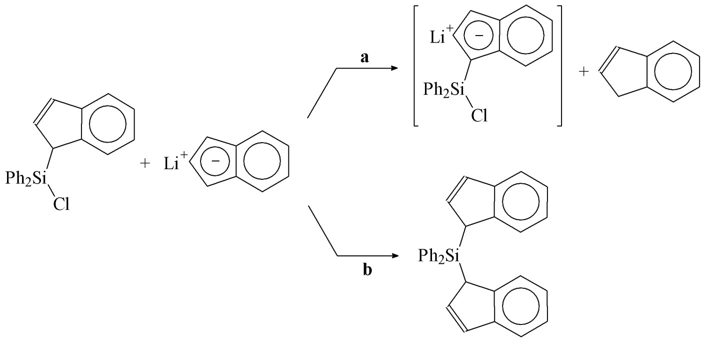


(3)

Table 1 ^{1}H and ^{13}C chemical shifts δ (ppm)[a] in NMR spectra of di(1*H*-inden-3-yl)diphenylsilane in $CDCl_3$

Fragment	Nucleus No.[b]	$\delta(^{1}H)$ (J/Hz)	$\delta(^{13}C)$[c]
Indenyl	1	3.53 (m)	41.21
	2	6.92 (t, $J_{HH} = 1.71$)	150.19
	4	7.23 (d, $J_{HH} = 7.57$)	123.37
	5	7.11 (t, $J_{HH} = 7.57$)	126.08
	6	7.18 (t, $J_{HH} = 7.32$)	124.36
	7		123.50
Phenyl	11,15	7.69 (m)	135.91
	12,14	7.35 (m)	127.93
	13	7.42 (m)	129.60

[a] Relative to TMS. [b] See atom numbering in eqn. 4. [c] Signals of quaternary atoms 3-C, 8-C, 9-C, and 10-C were not assigned: δ 147.96, 144.46, 140.15 and 134.16.

Table 2 Results of NOE for di(1*H*-inden-3-yl)diphenylsilane in $CDCl_3$

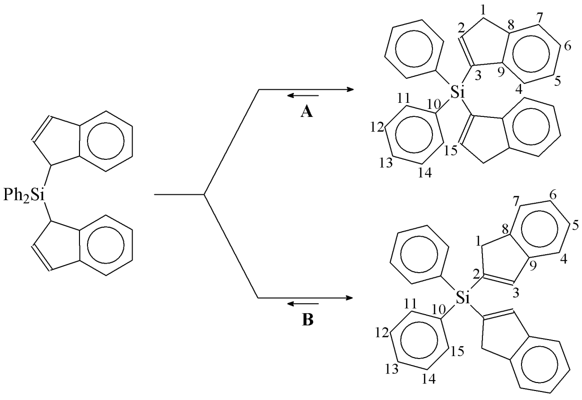
Irradiated nucleus[a]	% NOE[b](observed nucleus)
1-H	9.5 (2-H), 4.4 (7-H)
2-H	5.8 (1-H), 4.6 (11/15-H)
7-H	11.2 (6-H), 2.4 (1-H)
11/15-H	15.4 (12/14-H), 3.5 (4-H), 2.4 (2-H)

[a] See atom numbering in eqn. (4). [b] Calculated assuming 100% for the irradiated signal.[9,10]

at the expense of allylsilyl isomers.[8] Thus, possible structures for the above-mentioned symmetrical vinyl isomer are di(1*H*-inden-3-yl)diphenylsilane (eqn. 4, pathway **A**) or di(1*H*-inden-2-yl)diphenylsilane (pathway **B**).

To assign a correct structure to the obtained isomer, we have used ^{1}H and ^{13}C (APT, assigned proton test) NMR spectra and multipulse 2-D-COSY, HETCOR, and 1-D NOE experiments (Tables 1 and 2). The data confirm the di(1*H*-inden-3-yl)-diphenylsilane structure (eqn. 4, pathway **A**) for the compound formed. The evidence in favor of this conclusion is as follows. First, from both ^{1}H NMR spectra and NOE between the neighboring protons the molecule should include a $=CHCH_2$ fragment. Additionally, NOE was observed for H(2) and H(4) by irradiation of *ortho*-protons of phenyl rings, *i.e.* H(11) and H(15), while NOE for H(4) was not observed by irradiation of H(2).

$HfCl_2[Ph_2Si(\eta^5\text{-}C_9H_6)_2]$ **1**, (*rac*) and **2** (*meso*) were prepared *via* transmetallation reaction using the organotin reagent (eqn. 5).[11–13] Analytically pure *meso* complex **2** was isolated in 8.5% yield after crystallization from CH_2Cl_2–pentane. Crystallization from diethyl ether gave the respective *rac* isomer **1** in 15.5% yield. From the evidence of NMR spectra, the latter product was contaminated with *ca.* 15% of **2**.



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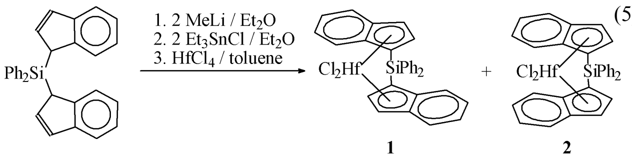


1 **2**

(5)

The use of NMR helped to resolve the structures for complexes **1** and **2**. In the case of analogous *ansa* complexes with $SiMe_2$ and CMe_2 bridges the determination of the configuration, *rac* or *meso*, of the respective metallocenes was made by studying the upfield region of their ^{1}H or ^{13}C NMR spectra. The racemates have equivalent Me groups in the bridge. On the other hand the Me groups are not equivalent in the spectra of *meso* complexes. The analysis of spectra of complexes with a $SiPh_2$ bridge is more difficult due to an overlap of resonances due to protons of Ph fragments of the bridge and aromatic protons of the indenyl system. However, due to *equivalence* of Ph groups in the racemate **1** and *non-equivalence* of these groups in the *meso* complex the assignment can be accomplished (assuming free rotation about Si–C(10) and Si–C(10′) bonds). Whereas the resonance of H(11), H(15) of **1** appears at δ 8.109 (m, AA′ part of AA′BB′C system) the ^{1}H NMR spectrum of **2** displays two equivalent characteristic multiplets at δ 8.115 and 8.211 attributed to H(11), H(15) and H(11′), H(15′) of two non-equivalent Ph fragments (AA′BB′C and DD′EE′F spin systems).

The second problem under investigation is the synthesis of the unsymmetrical sterically hindered complex $HfCl_2[Ph_2Si(\eta^5\text{-}$

Table 3 ^1H and ^{13}C chemical shifts δ (ppm)[a] and spin–spin coupling constants J_{HH}/Hz in NMR spectra of complex **3** in CD_2Cl_2

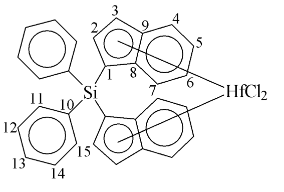
Fragment	Nucleus No.[b]	$\delta(^1H)$[c] (J/Hz)	$\delta(^{13}C)$[d]
Cyclopentadienyl	1		102.79
	2, 5	5.96	110.25
	3, 4	6.65	124.41
Fluorenyl	6		63.26
	7, 18		127.41
	8, 17	6.91 (J_{HH} = 8.61)	124.51
	9, 16	7.03 (J_{HH} = 8.61, J 6.84)	128.60
	10, 15	7.60 (J_{HH} = 8.32, J 6.84)	126.85
	11, 14	8.11 (J_{HH} = 8.38)	124.78
	12, 13		128.94
Phenyl	19		133.02
	20, 24	8.16	134.71
	21, 23	7.58	129.24
	22	7.61	131.27

[a] Relative to TMS. [b] See atom numbering in eqn. (7). [c] Chemical shifts for 10/15-H, 21/23-H, and 22-H were obtained from the respective projections in the HETCOR spectrum, the chemical shift and $^3J_{HH}$ for 10/15-H from NOE (irradiation of 9/16-H). [d] Signals for 7/18-C, 10/15-C, 12/13-C, 19-C, and 22-C were assigned on the basis of their multiplicity in selective double heteronuclear resonance ^{13}C-$\{^1H\}$ [15] by suppression of 8/17-H and 9/16-H with 40H power.

Table 4 Results of NOE for complex **3** in CD_2Cl_2

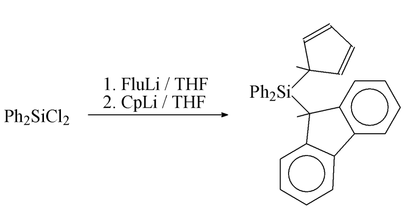
Irradiated nucleus[a]	% NOE[b] (observed nucleus)
2/5-H	15.5 (3/4-H), 13.9 (20/24-H), 6.9 (8/17-H)
3/4-H	11.4 (8/17-H)
9/16-H	16.3 (10/15-H), 13.1 (8/17-H)
20/24-H	16.7 (21/23-H), 7.2 (2/5-H), 4.5 (8/17-H)

[a] See atom numbering in eqn. (7). [b] Calculated assuming 100% for the irradiated signal.[9,10]



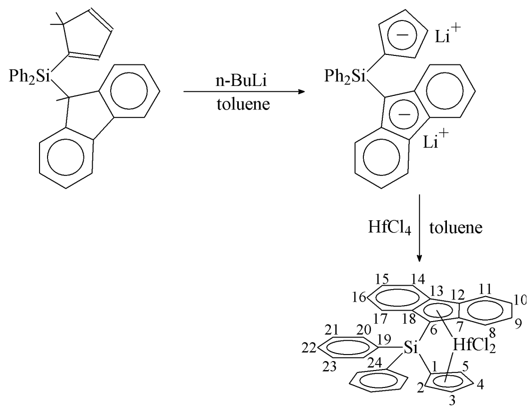
$C_{13}H_8)(\eta^5$-$C_5H_4)]$ **3**. Cyclopentadienyl(fluoren-9-yl)diphenylsilane (a mixture of isomers) has been synthesized by treatment of Ph_2SiCl_2 with fluorenyllithium, followed by cyclopentadienyllithium (eqn. 6). This method gave the desired product in 28.5% yield. In this case the side metallation of the formed chlorofluorenyldiphenylsilane by CpLi is impossible.[14] So, a low basicity of CpLi favors nucleophilic substitution at silicon atom and high yield synthesis of the desired ligand. The *ansa* complex **3** was prepared by treatment of $HfCl_4$ with 1 equivalent of the dilithium salt of the ligand in toluene (eqn. 7). This compound was isolated as a yellow crystalline solid in 62% yield.

(6)



The structure of compound **3** was established by NMR spectroscopy (Tables 3 and 4). An assignment was made using 2-D spectra (COSY, HETCOR), 1-D NOE, and selective double resonance ^{13}C-$\{^1H\}$ experiments (see Table 3 for experimental details). It is of interest that the resonance of the quarternary C(6) atom of the fluorenyl fragment is at δ 63.26, *i.e.* typical for a sp^3 carbon, which can be interpreted as evidence in favor of σ bonding of this carbon with hafnium (see also ref. 16). Crystallographic data, supporting this conclusion, are presented in the next section.

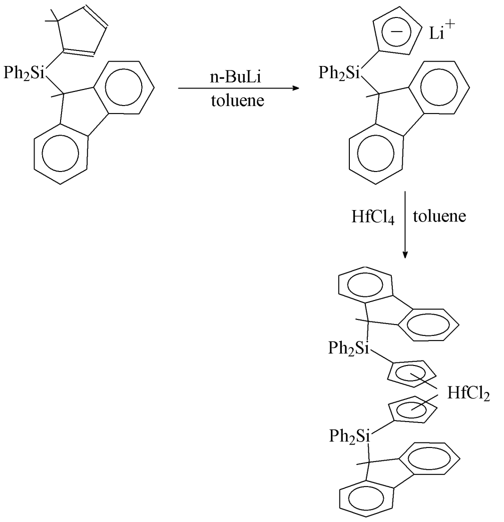
(7)



3

From the evidence of NMR, if an excess of ligand is used the synthesis of complex **3** is complicated by the formation of by-product, which was characterized by crystal structure analysis to be a complex derived from two mono-metallated cyclopentadienyl(fluoren-9-yl)diphenylsilane molecules (eqn. 8).

(8)



4

Molecular structures of $HfCl_2[Ph_2Si(\eta^5$-$C_{13}H_8)(\eta^5$-$C_5H_4)]$ 3 and $HfCl_2[Ph_2Si(C_{13}H_9)(\eta^5$-$C_5H_4)]_2$ 4

Complexes **3** and **4** were characterized by crystal structure analysis.The molecular structure of bridged *ansa*-hafnocene **3** is shown in Fig. 1. Bond lengths are given in Table 5. The asymmetric unit contains one independent molecule of hafnocene **3** and one solvent dichloromethane molecule. Complex **3** possesses an approximate mirror plane symmetry. The values of the Hf–Cl distances and Cl–Hf–Cl angle (2.398(3), 2.411(3) Å and 96.4(1)°) are comparable with those found for the closely related compound $HfCl_2(\eta^5$-$C_5H_4CPh_2$-η^5-$C_{13}H_8)$ (2.403(2) Å and 95.6°).[17] It is of interest that the inclusion of the short bridging group $SiPh_2$ between cyclopentadienyl and fluorenyl ligands does not distort significantly the metallocene moiety. Thus, in the structure of **3** the angle formed by the centroids of C5 rings and Hf atom is equal to 129.8°. On the other hand, Si(1)–C(1) and Si(1)–C(6) bonds are inclined to the least squares planes of C5 rings by 21.2 and 13.8°, respectively. The latter results in a decrease of the C(1)–Si(1)–C(6) angle to 96.3°. The Hf–C(6) distance (2.44(1) Å) is much shorter than Hf–C(12) and Hf–C(13) (2.75(2) and

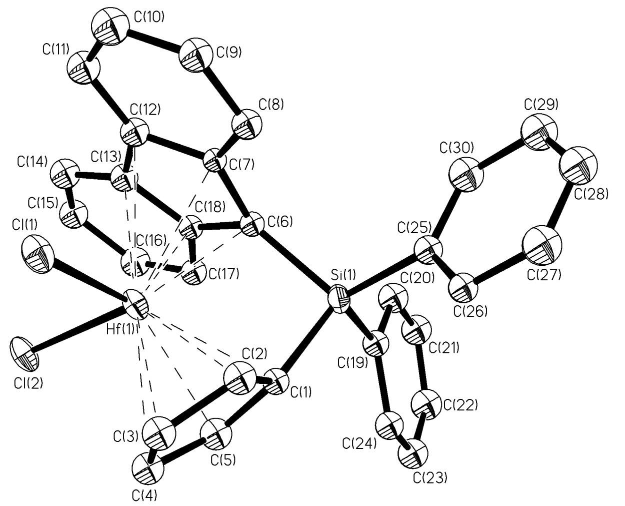


Fig. 1 View of complex **3**.

Table 5 Bond lengths (Å) for complex **3**

Hf(1)–Cl(1)	2.398(3)	C(7)–C(8)	1.45(2)
Hf(1)–Cl(2)	2.411(3)	C(8)–C(9)	1.36(2)
Hf(1)–C(5)	2.45(2)	C(8)–C(10)	1.42(2)
Hf(1)–C(6)	2.437(12)	C(10)–C(11)	1.36(2)
Hf(1)–C(2)	2.46(2)	C(11)–C(12)	1.41(2)
Hf(1)–C(1)	2.48(2)	C(12)–C(13)	1.43(2)
Hf(1)–C(3)	2.51(2)	C(13)–C(14)	1.41(2)
Hf(1)–C(4)	2.52(2)	C(13)–C(18)	1.40(2)
Hf(1)–C(7)	2.552(13)	C(14)–C(15)	1.36(2)
Hf(1)–C(18)	2.566(13)	C(15)–C(16)	1.40(2)
Hf(1)–C(13)	2.73(2)	C(16)–C(17)	1.38(2)
Hf(1)–C(12)	2.75(2)	C(17)–C(18)	1.43(2)
Si(1)–C(1)	1.848(13)	C(19)–C(20)	1.41(2)
Si(1)–C(19)	1.874(14)	C(19)–C(24)	1.40(2)
Si(1)–C(25)	1.868(13)	C(20)–C(21)	1.39(2)
Si(1)–C(6)	1.86(2)	C(21)–C(22)	1.37(2)
C(1)–C(2)	1.44(2)	C(22)–C(23)	1.37(2)
C(1)–C(5)	1.46(2)	C(23)–C(24)	1.38(2)
C(2)–C(3)	1.42(2)	C(25)–C(26)	1.38(2)
C(3)–C(4)	1.41(2)	C(25)–C(30)	1.40(2)
C(4)–C(5)	1.44(2)	C(26)–C(27)	1.42(2)
C(6)–C(18)	1.48(2)	C(27)–C(28)	1.37(2)
C(6)–C(7)	1.48(2)	C(28)–C(29)	1.36(2)
C(7)–C(12)	1.43(2)	C(29)–C(30)	1.41(2)

2.73(2) Å). The same Zr–fluorenyl bonding is common for *ansa*-zirconocene derivatives.[17,18]

Fig. 2 shows the structure and atom numbering scheme for compound **4**. Bond lengths are given in Table 6. The asymmetric unit contains one independent molecule of **4** and two disordered dichloromethane molecules, one of which occupies an inversion center. The coordination environment of Hf has a bent sandwich geometry with two chloride ligands lying in the bisecting plane. Both cyclopentadienyl rings are planar within 0.012 and 0.005 Å. The Hf–Cl and Hf–Cp_{cent} distances are equal to 2.424(2), 2.413(2) and 2.188, 2.193 Å, respectively. The Cl–Hf–Cl and Cp_{cent}–Hf–Cp_{cent} angles are 94.29(6) and 129.5°. Analysis of the Cambridge Structural Database (Release 5.18[19]) shows that the geometry of the central metallocene fragment in **4** is common for biscyclopentadienyldichlorohafnium derivatives (13 entries, excluding short bridged *ansa* compounds). Thus, the Hf–Cl, Hf–Cp_{cent} distances and Cl–Hf–Cl, Cp_{cent}–Hf–Cp_{cent} angles lie within the ranges 2.410–2.431, 2.166–2.207 Å and 92.85–97.64, 125.67–132.42°, respectively. Both silyl substituents in **4** are oriented towards the opposite lateral sectors of the metallocene moiety (looking down the line through the Cp ring centroids). The same *anti* conformation was previously shown to be characteristic for $Zr(RC_5H_4)_2(X)_2$ (X = halide) derivatives with bulky R substituents.[20,21] The Si(1) and Si(1′) atoms deviate slightly (0.268, 0.301 Å) from the least squares planes of the corresponding Cp rings in the directions opposite to the Hf atom. The latter are probably caused by steric interactions of the bulky silyl substituents with the opposite Cp rings. Both Si atoms possess distorted tetrahedral coordination with C–Si–C angles lying in the range 102.8(3)–119.1(3)°. The rotations of the silyl substituents around Si–C(Cp) bonds are different. The latter makes the whole molecule asymmetric. Both fluorenyl fragments

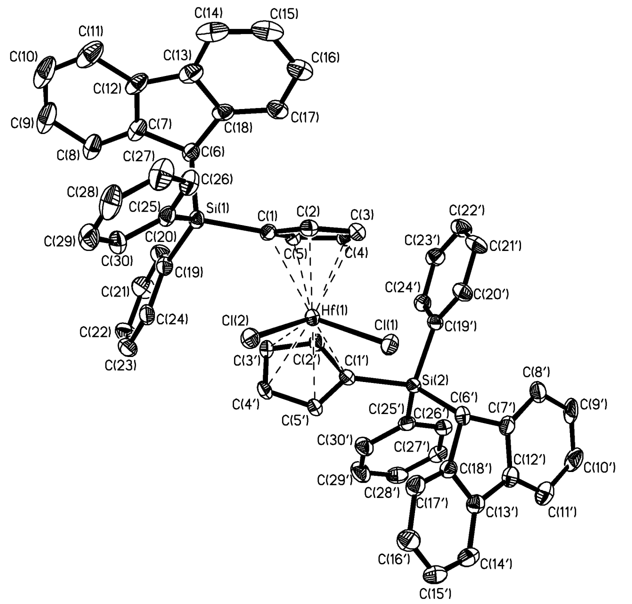


Fig. 2 View of complex **4**.

Table 6 Bond lengths (Å) for complex **4**

Hf(1)–Cl(2)	2.413(2)	C(20)–C(21)	1.379(11)
Hf(1)–Cl(1)	2.424(2)	C(21)–C(22)	1.396(11)
Hf(1)–C(2′)	2.471(6)	C(22)–C(23)	1.378(11)
Hf(1)–C(1)	2.489(5)	C(23)–C(24)	1.390(10)
Hf(1)–C(5)	2.497(6)	C(25)–C(26)	1.400(10)
Hf(1)–C(3′)	2.491(7)	C(25)–C(30)	1.404(9)
Hf(1)–C(4)	2.496(6)	C(26)–C(27)	1.397(11)
Hf(1)–C(1′)	2.504(6)	C(27)–C(28)	1.374(13)
Hf(1)–C(2)	2.500(6)	C(28)–C(29)	1.396(13)
Hf(1)–C(3)	2.515(6)	C(29)–C(30)	1.385(10)
Hf(1)–C(5′)	2.523(6)	C(1′)–C(2′)	1.416(9)
Hf(1)–C(4′)	2.530(6)	C(1′)–C(5′)	1.422(8)
Si(1)–C(25)	1.875(6)	C(2′)–C(3′)	1.425(8)
Si(1)–C(19)	1.884(7)	C(3′)–C(4′)	1.426(10)
Si(1)–C(1)	1.877(6)	C(4′)–C(5′)	1.413(9)
Si(1)–C(6)	1.924(6)	C(6′)–C(18′)	1.505(9)
Si(2)–C(19′)	1.882(6)	C(6′)–C(7′)	1.528(8)
Si(2)–C(1′)	1.889(6)	C(7′)–C(8′)	1.390(10)
Si(2)–C(25′)	1.896(6)	C(7′)–C(12′)	1.407(10)
Si(2)–C(6′)	1.927(6)	C(8′)–C(9′)	1.402(10)
C(1)–C(5)	1.422(8)	C(9′)–C(10′)	1.383(12)
C(1)–C(2)	1.429(9)	C(10′)–C(11′)	1.390(12)
C(2)–C(3)	1.412(9)	C(11′)–C(12′)	1.400(10)
C(3)–C(4)	1.411(10)	C(12′)–C(13′)	1.449(9)
C(4)–C(5)	1.425(9)	C(13′)–C(18′)	1.407(9)
C(6)–C(18)	1.508(10)	C(13′)–C(14′)	1.409(10)
C(6)–C(7)	1.513(9)	C(14′)–C(15′)	1.372(12)
C(7)–C(12)	1.413(11)	C(15′)–C(16′)	1.401(12)
C(7)–C(8)	1.394(11)	C(16′)–C(17′)	1.405(10)
C(8)–C(9)	1.405(11)	C(17′)–C(18′)	1.389(9)
C(9)–C(10)	1.37(2)	C(19′)–C(24′)	1.387(9)
C(10)–C(11)	1.39(2)	C(19′)–C(20′)	1.406(9)
C(11)–C(12)	1.400(10)	C(20′)–C(21′)	1.391(9)
C(12)–C(13)	1.470(12)	C(21′)–C(22′)	1.402(11)
C(13)–C(18)	1.403(9)	C(22′)–C(23′)	1.371(11)
C(13)–C(14)	1.398(12)	C(23′)–C(24′)	1.392(9)
C(14)–C(15)	1.372(14)	C(25′)–C(26′)	1.390(9)
C(15)–C(16)	1.418(13)	C(25′)–C(30′)	1.400(9)
C(16)–C(17)	1.387(11)	C(26′)–C(27′)	1.394(9)
C(17)–C(18)	1.401(10)	C(27′)–C(28′)	1.375(10)
C(19)–C(24)	1.414(9)	C(28′)–C(29′)	1.379(11)
C(19)–C(20)	1.399(10)	C(29′)–C(30′)	1.391(10)

C(6)–C(18) and C(6′)–C(18′) are planar within 0.121 and 0.185 Å.

3 Experimental

All manipulations have been done either on a high-vacuum line in an all-glass apparatus equipped with polytetrafluoroethylene stopcocks or in an atmosphere of thoroughly purified argon using the standard Shlenk technique. THF was distilled over $LiAlH_4$. Toluene and pentane were distilled over Na/K alloy and kept over CaH_2. CH_2Cl_2, as well $CDCl_3$ and CD_2Cl_2, were distilled over P_4O_{10} and kept over 3A molecular sieves. ^1H and ^{13}C NMR spectra were recorded with a Bruker AM 360 spectrometer.

Preparations

Di(1*H*-inden-1-yl)diphenylsilane. To a solution of indenyllithium (prepared from 13.0 ml (11.62 g, 0.10 mol) of indene in 120 ml of THF and 52.0 ml of 1.43 M MeLi in diethyl ether) was added dropwise for several minutes at −60 °C a solution of 10.5 ml (12.66 g, 0.05 mol) Ph_2SiCl_2 in 50 ml of THF. The mixture was stirred at this temperature for 3 h, followed by overnight at ambient temperature, and finally evaporated to dryness. The residue was dissolved in 200 ml of toluene and filtered. The toluene solution was evaporated to dryness and the product extracted with 500 ml of warm pentane. The white solid obtained from the pentane solution at −30 °C was filtered off and dried in vacuum. This procedure gave 4.28 g (21%) of a *rac*/*meso* mixture of di(1*H*-inden-1-yl)diphenylsilanes.

***rac*- and *meso*-$HfCl_2[Ph_2Si(\eta^5\text{-}C_9H_6)_2]$ 1 and 2.** To a suspension of 3.66 g (8.87 mmol) of di(1*H*-inden-1-yl)diphenylsilane in 100 ml of ether 10.0 ml, 1.86 M MeLi in ether was added dropwise for several minutes. This mixture was stirred for 2 h. Then a solution of 4.28 g (17.7 mmol) $SnEt_3Cl$ in 70 ml of ether was added dropwise for several minutes. The mixture was stirred for 1 hour and evaporated to dryness in vacuum. The residue was redissolved in 100 ml of toluene and evaporated to dryness to remove traces of ether. A new portion of 100 ml of toluene was added and the mixture filtered. The resultant toluene solution was added dropwise for 2 h to a suspension of 2.84 g (8.87 mmol) $HfCl_4$ in 50 ml of toluene. This mixture was stirred for 6 h at 95 °C. A yellow precipitate obtained at 0 °C was filtered off, washed by 3 × 15 ml of cold toluene, then by 2 × 50 ml of ether. The ether extracts were combined and evaporated to *ca.* 30 ml. Yellow *rac* complex **1** which precipitated at −30 °C was filtered off and dried in vacuum. Yield 0.91 g (15.5%). The yellowish brown solid residue (after extraction with toluene and ether) was dissolved in 50 ml of CH_2Cl_2 and filtered through a G4 frit filter. To this solution 50 ml of pentane were added. The yellow solid which precipitated at −30 °C was filtered off and dried in vacuum. This procedure gave 0.50 g (8.5%) of *meso* complex **2**.

Chloro(fluoren-9-yl)diphenylsilane. A solution of fluorenyllithium (prepared from 15.3 g (90 mmol) of fluorene in 200 ml of THF and 39 ml of 2.3 M n-BuLi in hexanes) was added dropwise for 5 h to a solution of 27 ml (32.5 g, 128 mmol) Ph_2SiCl_2 in 100 ml THF. This mixture was stirred overnight at rt, then, evaporated to dryness. The red oil was washed with 250 ml of dry hexane. The extract was filtered. Crystallization at −30 °C gave 26 g (75%) of a yellowish solid.

Cyclopentadienyl(fluoren-9-yl)diphenylsilane. To a solution of C_5H_5Li (prepared from 9.92 g (150 mmol) of freshly distilled cyclopentadiene and 65 ml of a 2.3 M solution of n-BuLi in hexanes in 200 ml THF) 11.5 g (30 mmol) of chloro(fluoren-9-yl)diphenylsilane in 100 ml of THF were added dropwise for 2 h at rt. This mixture was stirred overnight at rt, treated with 50 ml of water and neutralized with 10% HCl. The organic layer was separated, dried over $MgSO_4$, evaporated to give an orange solid, which was washed with hot hexane and extracted with 3 × 150 ml of hot methanol. The resulting white solid was dried in vacuum. Yield: 4.71 g (38%).

Table 7 Crystal data, data collection, structure solution and refinement parameters for complexes **3** and **4**

	3	**4**
Empirical formula	$C_{30}H_{22}Cl_2HfSI\cdot CH_2Cl_2$	$C_{60}H_{46}Cl_2HfSi_2\cdot 1.5CH_2Cl_2$
Formula weight	744.8	1199.93
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a/Å	11.0830(2)	13.5860(9)
b/Å	8.9801(2)	14.0886(6)
c/Å	28.7654(6)	15.9919(6)
α/°		69.997(1)
β/°	101.096(1)	71.314(2)
γ/°		89.535(1)
V/Å^3	2809.4(1)	2706.9(2)
Z	4	2
μ/mm^{-1}	4.157	2.257
T/K	150.0(2)	150.0(2)
Reflections collected	11778	19863
Independent reflections	3487 [R_{int} = 0.1223]	12276 [R_{int} = 0.0639]
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0620, 0.1348	0.0589, 0.1489
(all data)	0.0957, 0.1679	0.0762, 0.2142

$HfCl_2[Ph_2Si(\eta^5\text{-}C_{13}H_8)(\eta^5\text{-}C_5H_4)]$ 3. To 11.4 g (27.6 mmol) of cyclopentadienyl(fluoren-9-yl)diphenylsilane in 300 ml of toluene 22.1 ml a 2.5 M solution of n-BuLi in hexanes was added dropwise. This mixture was refluxed for 1 h and cooled to −40 °C. At this temperature 9.0 g (28.0 mmol) of $HfCl_4$ were added. The resulting mixture was refluxed for 4 h, cooled and filtered. The precipitate was washed with 4 × 70 ml of toluene. The combined toluene fractions were evaporated to *ca.* 300 ml. Crystallization at −30 °C gave a yellow-orange crystalline solid which was separated and dried in vacuum. The crude product was recrystallized from hexane–CH_2Cl_2 (1 : 1). Yield: 11.3 g (62%).

X-Ray diffraction study of complexes 3 and 4

Crystal data, data collection, structure solution and refinement parameters for compounds **4** and **3** are given in Table 7. For the structure of **4** all non hydrogen atoms (except solvent dichloromethane molecules) were refined with anisotropic thermal parameters. For compound **3**, hafnium, chlorine and silicon atoms were refined anisotropically and all carbon atoms, in an isotropic approximation. For both structures, hydrogen atoms were placed in calculated positions and refined using a riding model.

CCDC reference numbers 152545 and 152546.

See http://www.rsc.org/suppdata/dt/b0/b009280k/ for crystallographic data in CIF or other electronic format.

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