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Synthesis and characterization of *ansa*-[1,1-bis(inden-1,1-diyl)-1-silacyclopentane]zirconium dichlorides. Crystal structures of *meso*- and *racemic*-[1,1-bis[inden-1,1-diyl)-1-silacyclopentane]-dichloro zirconium and *racemic*-[1,1-bis(4,5,6,7-tetrahydroinden-1,1-diyl)-1-sila-cylopentane]dichlorozirconium

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Abstract

The reaction of 1-silacyclopentylbis(1-indenyl) with two equivalents of BuLi gives the di-anion $(CH_2)_4Si(C_9H_6)_2^{2-}$, which with $ZrCl_4$ gives the *ansa*-metallocene dichlorides *racemic*- and *meso*- $(CH_2)_4Si(C_9H_6)_2ZrCl_2$ (**1a**, **1b**). Hydrogenation of **1a** yields *racemic*- $(CH_2)_4Si(C_9H_{10})$ZrCl2 (**2**). The structure of **1a**, **1b** and **2** have been obtained by X-ray diffraction studies. Both **1a** and **2** show the expected C_2-axial symmetry.

Keywords: Zirconium; Silacyclopentyl; Indenyl; Crystal structure; *Ansa*-bridging; Metallocenes

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1. Introduction

Chiral complexes of Group 4 transition metals incorporating two appropriately substituted cyclopentadienyl ligands are finding increasing application [1] in enantioselective synthesis [2] and stereoselective polymerization [3]. An excellent review [1] has appeared and theoretical studies concerning structural variations and tacticity control [4], as well as the role of agostic hydrogen interactions [5], have been reported. The most stereoselective species are found among bridged *ansa*-metallocenes in which the two indenyl, tetrahydroindenyl, or otherwise-substituted cyclopentadienyl groups are linked by a bridge between the 1 and 1′ positions [3]. The catalytic species of α-olefin polymerization derived from Group 4 metallocene precursors is the 14-electron $3d^0$ cation [3]. It is generated by mixing the metallocene dichloride with a large excess of methylalumoxane [6], or by a nearly stoichiometric reaction of a metallocene dialkyl with an activator such as $[C_6H_5(CH_3)_2NH^+][B(C_6F_5)_4^-]$ [7], $[(C_6H_5)_3C^+][B(C_6F_5)_4^-]$ [8], or $B(C_6F_5)_3$ [9]. Lewis base-adducts of cationic Group 4 metallocene alkyls, single component catalysts, have been reported [10]. We describe here the synthesis, characterization and crystal structures of *rac*-, *meso*-1-silacyclopentylbis(1-indenyl)zirconium dichloride (**1a**, **1b**) and *rac*-1-silacyclopentylbis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride (**2**). The polymerizations of propene, ethene and ethene–propene mixtures by **1a** have been described in detail by Tsai and Chien [11].

2. Results and discussion

The synthesis of **1a**, **1b** and **2** is outlined in Scheme 1. Double deprotonation of 1-silacyclopentylbis(1-indene) and subsequent reaction of the di-anion with $ZrCl_4$ gives the *ansa*-metallocenes **1a** and **1b**. The ^{1}H

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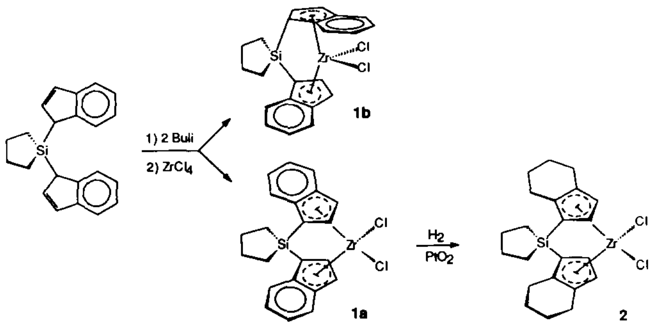

Scheme 1.

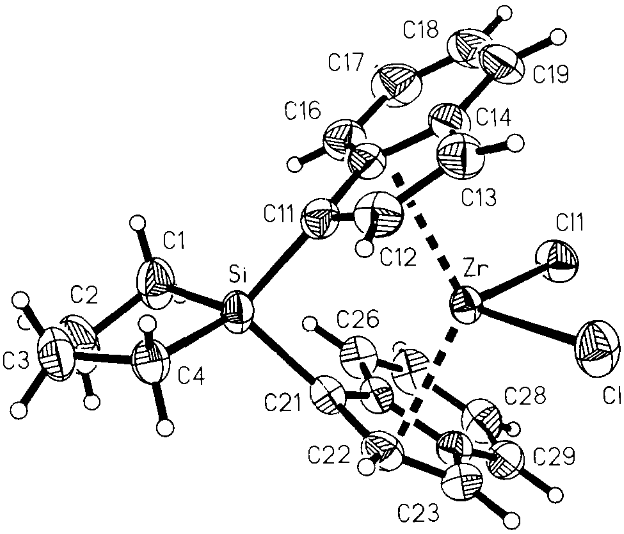

Fig. 2. Molecular structure of (*R*, *S*)-**1b**.

NMR spectra of **1a** and **1b** show the resonances of H_α at 6.08 ppm and 6.12 ppm and those of H_β at 6.88 and 6.95 ppm, respectively (H_α=C(12)-H, H_β=C(13)-H, vide infra). The values for **1a** correspond exactly to those reported for the dimethylsilyl-bridged analogue [12]. The ^{13}C spectra of **1a** and **1b** show the expected nine resonances for the indenyl groups. The silacyclopentyl ring in **1a** gives rise to two absorptions, at 27.2 and 12.4 ppm, for C(2), C(3) and C(1), C(4) respectively, as expected for a pair of enantiotopic methylene carbons in a C_2-symmetrical molecule. In the case of **1b**, however, C(1), C(2), C(3) and C(4) are magnetically non-equivalent and give rise to 4 absorptions, at 27.6, 26.0, 12.1 and 11.2 ppm, respectively, as expected for a pair of diastereotopic methylene carbons [13]. The ^1H NMR spectrum of **2** shows doublets from H_α and H_β at 5.46 and 6.64 ppm, values close to those found for the dimethylsilyl-bridged analogue [14]. The enantiotopic pair of methylene carbons of the silacyclopentyl ring in **2** show the expected two resonances for C(1), C(4) and C(2), C(3); at 11.4 and 26.7 ppm, respectively.

The molecular structures of **1a**, **1b** and **2** are shown in Figs. 1–3. All three complexes show the expected geometry, with planar C_5-rings, the average deviations from planarity being 0.01 Å complexes **1a** and **2** adopt the C_2 symmetrical conformation. The symmetry axis bisecting the Cl–Zr–Cl angles is almost perfectly maintained, although the molecules are not situated on a crystallographic C_2 axis. The coordination sites are framed in an equivalent fashion, in accordance with the requirements for equivalent enantiofacial coordination of prochiral substrates. In **1b** the two chloride ligands, and hence the two coordination sites, are inequivalent, one of them being sterically hindered by the benzo-units from both top and bottom whereas the other is essentially unencumbered. The geometry of **1a** deviates only slightly from that of the dimethylsilyl-bridged analogue. A striking feature, however, is the

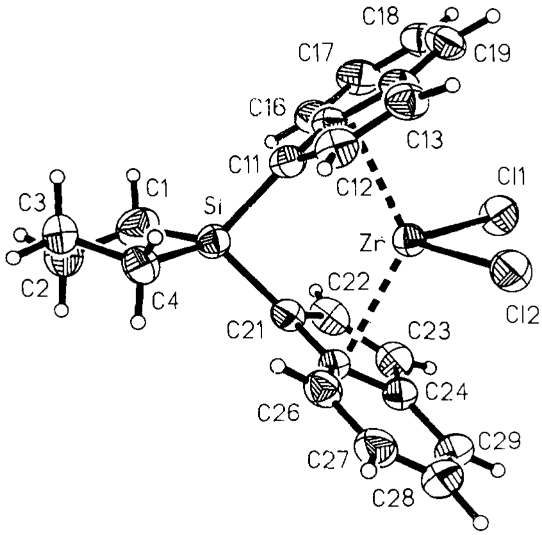

Fig. 1. Molecular structure of (*S*, *S*)-**1a**.

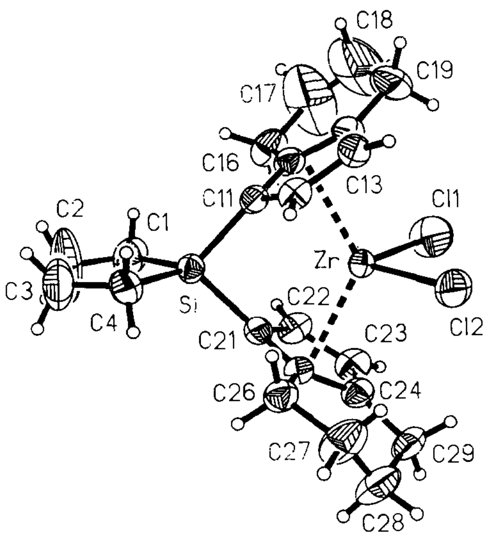

Fig. 3. Molecular structure of (*R*, *R*)-**2**.

enlargement of the Cp(1)–Zr–Cp(2) angle by approximately 7°, caused by strain introduced by the silacyclopentyl ring. The C(1)–Si–C(4) angle is approximately 15° smaller than the CH_3–Si–CH_3 angle in the corresponding dimethylsilyl-bridged analogue, and causes an increased stereorigidity in the molecule, as is clearly demonstrated by the polymerization behaviour of **1a** [11]. Changes of the substituents in silicon bridged metallocenes do alter their chemical behaviour, as was also observed for changes in the bridge of (η^5-$C_5H_4CR_2$-η^5-$C_{13}H_8$)MCl_2 (M=Zr, Hf; R=CH_3, [15], C_6H_6 [16]) complexes.

3. Experimental section

Reactions with organometallic compounds were carried out under argon in Schlenk-type glassware. Solvents were dried and distilled under argon prior to use. 1,1′-Dichloro-1-silacyclopentane was purchased from ABCR and was distilled under argon prior to use, and 1,1-di(1-indenyl)-1-silacyclopentane was prepared as previously reported [11]. Hydrogenations were carried out in a 250 ml Berghof BAR 845 pressure vessel. The NMR-spectra were recorded with a Jeol GX 400 (^1H: 400 MHz, ^{13}C: 100.6 MHz) NMR spectrometer with Me_4Si as internal standard. Direct inlet electron ionization mass spectra (EIMS) were obtained at 70 eV with a VG-7070E mass spectrometer.

3.1. X-ray structure determinations

Details of crystal parameters, data collection parameters and refined data for **1a**, **1b** and **2** are summarized in Table 1. Intensity measurements were made on a Nicolet R3m diffractometer using graphite-monochromatized Mo Kα radiation. Monitoring of two intensity check reflections showed no crystal decay during data collection. The data sets were corrected for Lorentz and polarization factors. Empirical absorption corrections were made from Ψ-scan data for **1a** and **1b**.

The crystal structures were determined by direct methods and subsequent Fourier synthesis using the SHELXTL program package [17]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions with fixed isotropic thermal parameters (C–H 0.96 Å and U 0.08 Å^2). For **2** the values of R and wR for the alternative absolute structure were practically the same (R 0.037 and wR 0.044). Selected bond lengths and angles are presented in Table 2, and the final atomic coordinates in Tables 3–5. Complete lists of bond lengths and angles and tables of hydrogen atom coordinates and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Table 1
Crystallographic data for **1a**, **1b** and **2**

	1a	**1b**	**2**
Formula weight	474.62	474.62	482.68
Crystal system	monoclinic	triclinic	orthorhombic
Space group	$P2_1/c$	P-1	$P2_12_12_1$
a (Å)	7.594(2)	10.193(2)	10.552(2)
b (Å)	24.671(9)	10.416(2)	12.130(3)
c (Å)	10.684(4)	10.467(2)	17.030(4)
α (deg)	90	64.04(1)	90
β (deg)	97.73(3)	86.35(2)	90
γ (deg)	90	85.22(2)	90
Z	4	2	4
V (Å^3)	1983(1)	995.2(5)	2179.8(9)
μ (mm^{-1})	0.88	0.88	0.80
F(000)	960	480	992
D_c (g cm^{-3})	1.589	1.584	1.471
Radiation	Mo Kα	Mo Kα	Mo Kα
Crystal dimensions (mm)	0.10 × 0.20 × 0.50	0.20 × 0.30 × 0.45	0.30 × 0.30 × 0.35
2θ limits (deg)	5–55	5–65	5–65
Scan mode	ω	ω	ω
Scan speed (deg/min)	2.44–29.3	2.44–29.3	2.44–29.3
Scan width (deg)	1.4	1.6	1.6
Unique reflections	4620	7248	4405
Observed reflections ($I > n\sigma(I)$)	3099 (n=2)	5348 (n=3)	2964 (n=3)
Number of variables	235	235	235
R	0.039	0.032	0.036
wR	0.041	0.040	0.043
$(\Delta\rho)_{max}/(\Delta\rho)_{min}$	0.44/ − 0.55	0.64/ − 0.67	0.49/ − 0.35

$R=\Sigma||F_0|-|F_c||/\Sigma|F_0|$, $w=1/(\sigma^2(F)+0.0005\,F^2)$.

Table 2
Selected bond lengths (Å) and angles (°) in **1a**, **1b** and **2**

	1a	**1b**	**2**
Zr–Cl(1)	2.432(1)	2.405(1)	2.430(2)
Zr–Cl(2)	2.426(1)	2.450(1)	2.438(2)
Zr–C(11)	2.478(4)	2.492(3)	2.485(4)
Zr–C(12)	2.485(4)	2.478(3)	2.444(4)
Zr–C(13)	2.596(4)	2.562(3)	2.562(5)
Zr–C(14)	2.665(4)	2.659(3)	2.649(5)
Zr–C(15)	2.552(4)	2.587(3)	2.560(4)
Zr–C(21)	2.473(4)	2.468(2)	2.479(4)
Zr–C(22)	2.486(4)	2.477(2)	2.442(4)
Zr–C(23)	2.625(4)	2.594(2)	2.550(4)
Zr–C(24)	2.693(4)	2.685(2)	2.635(4)
Zr–C(25)	2.556(4)	2.569(2)	2.550(4)
Zr–Cp(1)	2.247	2.248	2.236
Zr–Cp(2)	2.262	2.252	2.225
Si–C(11)	1.866(4)	1.868(2)	1.876(4)
Si–C(21)	1.856(4)	1.874(3)	1.876(4)
C(11)–C(12)	1.438(5)	1.434(4)	1.424(6)
C(12)–C(13)	1.400(6)	1.412(3)	1.427(6)
C(13)–C(14)	1.425(6)	1.417(4)	1.388(7)
C(14)–C(15)	1.439(5)	1.443(4)	1.426(6)
C(11)–C(15)	1.458(6)	1.450(3)	1.428(6)
C(21)–C(22)	1.434(6)	1.435(4)	1.427(6)
C(22)–C(23)	1.407(6)	1.409(4)	1.414(7)
C(23)–C(24)	1.420(6)	1.423(3)	1.394(6)
C(24)–C(25)	1.432(5)	1.445(4)	1.428(6)
C(21)–C(25)	1.458(5)	1.446(3)	1.439(5)
Cl(1)–Zr–Cl(2)	98.2(1)	97.3(1)	99.4(1)
Cp(1)–Zr–Cp(2)	127.6	127.7	126.5
C(11)–Si–C(21)	95.2(2)	95.4(1)	94.2(2)
C(1)–Si–C(4)	96.5(2)	96.7(1)	97.0(2)
C(1)–Si–C(21)	116.4(2)	116.5(1)	115.4(2)
C(4)–Si–C(21)	115.7(2)	112.9(1)	118.0(2)
C(1)–Si–C(11)	119.0(2)	117.5(1)	118.5(2)
C(4)–Si–C(11)	115.6(2)	119.2(1)	115.4(2)

Cp(1) and Cp(2) refer to the centroids of the C(11)–C(12)–C(13)–(14)–C(15) and C(21)–C(22)–C(23)–C(24)–C(25) rings respectively.

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for **2**

	x	y	z	U_{eq}
Zr	2065(1)	4363(1)	3126(1)	34(1)
Cl(1)	1326(2)	5437(2)	4240(1)	84(1)
Cl(2)	4082(1)	3722(1)	3654(1)	68(1)
Si	714(1)	3894(1)	1381(1)	36(1)
C(1)	−782(5)	4421(5)	917(3)	62(2)
C(2)	−757(9)	3879(10)	149(5)	147(5)
C(3)	238(7)	3212(7)	−85(4)	88(3)
C(4)	1240(5)	3011(4)	540(3)	54(2)
C(11)	603(4)	3177(3)	2354(2)	34(1)
C(12)	1606(4)	2507(3)	2646(3)	38(1)
C(13)	1452(5)	2378(4)	3473(3)	48(1)
C(14)	380(5)	2958(4)	3700(3)	48(1)
C(15)	−135(4)	3483(3)	3022(3)	40(1)
C(16)	−1354(4)	4130(5)	3054(3)	58(2)
C(17)	−1960(7)	4086(12)	3831(5)	157(6)
C(18)	−1530(9)	3471(12)	4434(6)	157(6)
C(19)	−250(6)	3012(6)	4494(3)	76(2)
C(21)	1833(4)	4981(3)	1746(2)	35(1)
C(22)	1442(4)	5859(3)	2248(3)	43(1)
C(23)	2517(5)	6306(3)	2628(3)	48(1)
C(24)	3588(4)	5729(4)	2380(4)	40(1)
C(25)	3182(3)	4886(3)	1852(3)	35(1)
C(26)	4094(4)	4143(4)	1419(3)	45(1)
C(27)	5455(5)	4303(6)	1715(4)	74(2)
C(28)	5795(5)	5434(5)	1903(4)	71(2)
C(29)	4976(5)	5947(4)	2546(3)	51(2)

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for **1b**

	x	y	z	U_{eq}
Zr	3217(1)	2506(1)	6795(1)	28(1)
Cl(1)	2481(1)	928(1)	9156(1)	42(1)
Cl(2)	4644(1)	3875(1)	7471(1)	50(1)
Si	2494(1)	2737(1)	3653(1)	34(1)
C(1)	1405(3)	1726(3)	3085(3)	52(1)
C(2)	1012(3)	2838(4)	1616(3)	67(1)
C(3)	2175(3)	3722(3)	824(3)	55(1)
C(4)	2962(2)	4093(3)	1821(2)	39(1)
C(11)	3823(2)	1686(2)	4918(2)	36(1)
C(12)	4963(2)	2277(3)	5138(3)	41(1)
C(13)	5476(2)	1383(3)	6486(3)	45(1)
C(14)	4712(2)	170(3)	7134(3)	41(1)
C(15)	3670(2)	356(2)	6184(2)	35(1)
C(16)	2746(3)	−718(3)	6577(3)	44(1)
C(17)	2896(3)	−1918(3)	7841(3)	56(1)
C(18)	3913(3)	−2087(3)	8769(3)	58(1)
C(19)	4802(3)	−1093(3)	8452(3)	52(1)
C(21)	1700(2)	3571(2)	4794(2)	32(1)
C(22)	2244(2)	4741(2)	4911(2)	36(1)
C(23)	1745(2)	4847(2)	6149(3)	38(1)
C(24)	820(2)	3780(2)	6830(2)	34(1)
C(25)	813(2)	2964(2)	6015(2)	31(1)
C(26)	−14(2)	1782(3)	6493(2)	40(1)
C(27)	−790(2)	1476(3)	7700(3)	46(1)
C(28)	−790(2)	2304(3)	8478(3)	48(1)
C(29)	−14(2)	3420(3)	8070(3)	42(1)

3.2. Synthesis of 1-silacyclopentylbis(1-indenyllithium).

An ice cold solution of 1,1′-di(1-indenyl)-1-silacyclopentane (18.5 g, 58.8 mmol) in 100 ml of diethyl ether was treated dropwise with butyllithium (47 ml, 2.5 M in hexanes, 117.5 mmol) and the mixture was stirred for two hours at ambient temperature. The diethyl ether was removed in vacuo and 50 ml pentane added. The white dilithium-salt was filtered off, washed twice with 50 ml pentane and dried in vacuo.

*3.3. Synthesis of racemic dichloride (**1a**) and the meso-dichloride (**1b**)*

A suspension of zirconium-tetrachloride (4.7 g, 20.2 mmol) in 50 ml of toluene was treated with 1-silacyclopentylbis(1-indenyllithium) (7.3 g, 22.4 mmol), added in portions. The mixture was stirred overnight, during which a dark red suspension formed. The toluene was evaporated off and the residue was ex-

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for **1a**

	x	y	z	U_{eq}
Zr	1572(1)	4053(1)	2822(1)	32(1)
Cl(1)	−1433(1)	4330(1)	3074(1)	48(1)
Cl(2)	2752(2)	4938(1)	2398(1)	49(1)
Si	3740(1)	2885(1)	2937(1)	37(1)
C(1)	3180(7)	2155(2)	3172(4)	57(2)
C(2)	4808(8)	1862(2)	2770(5)	68(2)
C(3)	6466(7)	2190(2)	3216(4)	62(2)
C(4)	6121(5)	2771(2)	2707(4)	48(1)
C(11)	3373(5)	3387(2)	4182(3)	37(1)
C(12)	4263(5)	3901(2)	4381(4)	42(1)
C(13)	3289(6)	4258(2)	5040(4)	44(1)
C(14)	1748(5)	3980(2)	5324(3)	40(1)
C(15)	1762(5)	3448(2)	4772(3)	35(1)
C(16)	327(6)	3083(2)	4882(4)	42(1)
C(17)	−987(6)	3250(2)	5547(4)	52(2)
C(18)	−991(6)	3770(2)	6110(4)	54(2)
C(19)	341(6)	4134(2)	6009(4)	49(1)
C(21)	2350(5)	3246(1)	1637(3)	35(1)
C(22)	447(5)	3274(2)	1470(4)	43(1)
C(23)	−165(5)	3710(2)	679(4)	46(1)
C(24)	1341(5)	3970(2)	292(3)	40(1)
C(25)	2894(5)	3700(1)	902(3)	33(1)
C(26)	4608(5)	3885(2)	699(4)	39(1)
C(27)	4719(7)	4294(2)	−149(4)	51(2)
C(28)	3180(7)	4544(2)	−779(4)	56(2)
C(29)	1517(7)	4404(2)	−573(4)	53(2)

tracted with 150 ml dichloromethane to leave lithium chloride. Concentration of the extract and cooling to −15°C gave bright orange microcrystals of **1a** (4.4 g, 9.3 mmol, 46%). Two subsequent crystallizations from the mother liquor at −30°C gave dark red **1b** (0.6 g, 1.3 mmol, 6%). In the mass spectrum of **1a**, parent ions of composition $C_{22}H_{20}SiZrCl_2^+$ were observed in the appropriate isotope ratios at m/e=472–480, corresponding to the base peak. In the mass spectrum of **1b**, parent ions of composition $C_{22}H_{20}SiZrCl_2^+$ were observed at m/e=472–480 in the appropriate isotope ratios. The base peak, however, corresponded to $C_{13}H_{15}Si^+$, at m/e=199.

^{1}H-NMR (CD_2Cl_2) **1a**: δ 7.58 (dt, 3J=8.7 Hz, ^4J=1.1 Hz, 2H), 7.49 (dq, ^3J=8.7 Hz, ^4J=1.1 Hz, 2H), 7.37 (ddd, ^3J=8.5, 6.7 Hz, ^4J=0.9 Hz, 2H), 7.08 (ddd, ^3J=8.7, 6.7 Hz, ^4J = 1.1 Hz, 2H), 6.88 (dd, ^3J=3.2 Hz, ^4J=1.1 Hz, 2H), 6.08 (d, ^3J=3.2 Hz, 2H), 2.32–2.22 (m, 2H), 1.90–1.62 (m, 6H).

^{13}C-NMR (CD_2Cl_2) **1a**: δ 133.8, 128.0, 127.0, 126.3, 126.0, 124.5, 118.2, 117.9, 88.6 27.2, 12.4.

^{1}H-NMR($CDCl_3$) **1b**: δ 7.53 (dt, ^3J=8.7 Hz, ^4J=0.9 Hz, 2H), 7.50 (dd, ^3J=8.7 Hz, ^4J=0.9 Hz, 2H), 7.21 (ddd, ^3J=8.7. 6.7 Hz, ^4J=0.9 Hz, 2H), 6.95 (dd, ^3J=3.2 Hz, ^4J=0.9 Hz, 2H), 6.12 (d, ^3J = 3.2 Hz, 2H), 2.18–2.10 (mt, ^3J = 7.2 Hz, 2H), 2.08–1.99 (mt, ^3J=7.2 Hz, 2H), 1.88 (t, ^3J=7.2 Hz, 2H) 1.53 (t, ^3J = 7.2 Hz, 2H).

^{13}C-NMR ($CDCl_3$) **1b**: 134.7, 127.9, 127.3, 126.1, 125.9, 125.4, 119.7, 119.2, 89.2, 27.6, 26.0, 12.1, 11.2.

*3.4. Synthesis of the racemic-1 (**2**).*

Compound **1a** (1.12 g, 2.3 mmol) containing PtO_2 (23 mg, 0.1 mmol) in 100 ml of dichloromethane was kept under hydrogen at 100 bar for 6 h. The pale green suspension was filtered through Celite and the solvent evaporated. Diffusion of a petroleum ether (b.p. 40–60°C) into a concentrated solution of the residue in toluene at −30°C yielded light green **2** (1.0 g, 2.0 mmol, 90%). The mass spectrum of **2** showed parent ions of composition $C_{22}H_{28}SiZrCl_2^+$ at m/e=480–488 in the appropriate isotope ratios. The base peak, however, corresponded to the fulvene complex $C_{22}H_{27}$-$SiZrCl^+$ (M^+-HCl), which gave the correct isotope ratios at m/e=444–452.

^{1}H NMR ($CDCl_3$) **2**: δ 6.64 (d, ^3J=3.0 Hz, 2H), 5.46 (d, ^3J = 3.0 Hz, 2H), 2.97 (ddd, ^3J=16.5, 9.5, 5.8 Hz, 2H), 2.70 (dt, ^3J=16.5, 5.0 Hz, 2H), 2.58 (ddd, ^3J=16.5, 9.5, 5.8 Hz, 2H), 2.28 (dt, ^3J=16.5, 5.0 Hz, 2H), 2.11–2.01 (m, 2H), 2.00–1.91 (m, 2H), 1.83–1.67 (m, 4H), 1.66–1.57 (m, 2H), 1.53–1.42 (m, 2H), 1.37–1.24 (m, 4H). ^{13}C NMR ($CDCl_3$) **2**: δ 138.4, 128.5, 125.1, 112.7, 101.3, 26.7, 26.1, 24.2, 22.2, 22.0, 11.4.

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