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Synthetic approach to 6-*tert*-butyl-5-methoxy-2-methylindenyl zirconium *ansa*-complexes, bridged in 4-position of indenyl fragment

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Experimental

All manipulations were performed under purified argon atmosphere. Metallocene synthesis was performed by using standard Schlenk technique. BuLi (1.6 M solution in hexanes) was used as purchased (Aldrich). Toluene, benzene, diethyl ether were refluxed with Na/benzophenone/dibenzo-18-crown-6, and distilled prior to use. Pentane and hexanes were refluxed over Na/K alloy for 12 hours, and then distilled. CH_2Cl_2 was washed with aqueous Na_2CO_3, stirred with $CaCl_2$ powder, refluxed over CaH_2 for 8 h and distilled. $CDCl_3$ was distilled over P_2O_5 and stored over 4 Å molecular sieves.

Preparation of 4-bromo-6-tert-butyl-5-methoxy-2-methylindan-1-ol. Indanone **9** (20 g, 70 mmol) was added by portions within 5 min to suspension of $NaBH_4$ (2.66 g, 70 mmol) in EtOH (150 ml). The mixture was heated under reflux with stirring for 1 h, stirred at room temperature for 16 h, poured into water (500 ml) and extracted with CH_2Cl_2 (4×200 ml). Combined organic phase was dried over $MgSO_4$, and evaporated. The yield 19.8 g (97%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.09 (m, 3H); 1.50 (d, 9H); 2.01-3.06 (m, 3H); 3.82 (d, 3H); 4.38 (s, 1H); 4.51-4.84 (dd, 1H); 7.44 (s, 1H). The product of ~90% purity (NMR) was used without purification.

*Preparation of [(4-bromo-6-tert-butyl-5-methoxy-2-methyl-2,3-dihydro-1H-inden-1-yl)-oxy](trimethyl)silane (**10**).* Triethylamine (10.2 ml, 73.5 mmol) was added to solution of 4-bromo-6-*tert*-butyl-5-methoxy-2-methylindan-1-ol (19.8 g, 63.9 mmol) in CH_2Cl_2 (150 ml). The mixture was cooled to -20 °C. Me_3SiCl (9.4 ml, 73.5 mmol) was added to it. After 16 h of stirring at room temperature, the mixture was washed with water (2×100 ml), dried over $MgSO_4$, passed through silica, and evaporated under reduced pressure. The yield 16.9 g (69%), pale yellow oil. For the mixture of diastereomers ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.23 (s),

0.27 (s) {$OSiMe_3$, total 9H}; 1.08 (d, ^3J = 6.9 Hz), 1.23 (d, ^3J = 6.8 Hz) {total 3H}; 1.41 (s, 9H); 2.29-3.17 (groups of m, 3H); 3.93 (d, 3H); 4.79 (d), 5.11 (d) {total 1H}; 7.19 (s); 7.22 (s) {total 1H}. $^{13}C\{^1H\}$ NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.27; 0.52; 14.2; 17.7; 30.80; 30.84; 35.35; 35.39; 38.96; 39.02; 39.7; 44.4; 61.4; 78.2; 83.4; 115.4; 115.7; 121.2; 121.9; 140.4; 140.7; 141.8; 142.9; 143.4; 156.3; 156.4. For $C_{18}H_{29}BrO_2Si$, 385.42, Calc.: C 56.09% H 7.58% O 8.30%. Found: C 56.31% H 7.88% O 8.11%

*Preparation of (5-tert-butyl-6-methoxy-2-methyl-1H-inden-7-yl)(9H-fluoren-9-yl)dimethyl-silane (**11**).* n-BuLi (2.8 ml of 2.5 M hexane solution, 7 mmol) was dropwise added to a cold (-60 °C) solution of **10** (2.5 g, 6.5 mmol) in Et_2O (13 ml). The reaction mixture was allowed to warm to 0 °C, and was cooled to -20 °C. A solution of chloro(fluoren-9-yl)dimethylsilane (1.85 g, 7.15 mmol) in Et_2O (5 ml) was added to it. The mixture was allowed to warm to room temperature. Solvent was evaporated under reduced pressure. The obtained residue was dissolved in benzene; *p*-toluenesulfonic acid (0.2 g) was added to the solution. The mixture was heated under reflux for 10 min, cooled to room temperature, washed with water (2×10 ml). Remaining solution was evaporated under reduced pressure. The product was obtained using column chromatography (Kieselgel 60, CH_2Cl_2/hexane 1:4). The yield 0.62 g (22%). ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.09 (s, 6H), 1.48 (s, 9H), 2.08 (s, 3H), 3.12 (s, 2H), 3.70 (s, 3H), 4.46 (s, 1H), 6,44 (s, 1H), 7.13 (m, 4H), 7.31 (t, 2H), 7.39 (s, 1H), 7.85 (d, 2H). $^{13}C\{^1H\}$ NMR (400 MHz, $CDCl_3$, 20 °C): δ = -2.0; 14.1; 16.6; 22.7; 31.7; 35.4; 41.7; 44.7; 64.8; 119.7; 120.9; 124.3; 125.2; 126.0; 126.4; 140.4; 140.7; 141.7; 145.1; 145.5; 149.0; 162.8. For $C_{30}H_{34}OSi$, 438.68, Calc.: C 82.14% H 7.81% O 3.65%. Found: C 82.44% H 8.04% O 3.55%.

*Preparation of bis(5-tert-butyl-6-methoxy-2-methyl-1H-inden-7-yl)(dimethyl)silane (**12**).* *n*-BuLi (8.9 ml of 1.6M hexane solution, 14.3 mmol) was dropwise added to a cold (-60 °C) solution of **8** (5.0 g, 13 mmol) in Et_2O (20 ml). The reaction mixture was allowed to warm to 0 °C, cooled to -20 °C. A solution of $SiMe_2Cl_2$ (0.86 g, 6.63 mmol) in Et_2O (10 ml) was added to it. The mixture was allowed to warm to room temperature. The solvent was evaporated under reduced pressure; the residue was dissolved in benzene; *p*-toluenesulfonic acid (0.2 g) was added into the solution. The mixture was heated under reflux for 10 min, cooled to room temperature, washed with water (2×10 ml); the solvent was evaporated. The product was obtained using column chromatography (Kieselgel 60, CH_2Cl_2/hexane 1:4). The yield was 0.4 g (13%), pale yellow solid. ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.97 (s, 6H); 1.47 (s, 18H); 1.93 (s, 6H); 2.73 (bs, 4H); 3.68 (s, 6H); 6.27 (bs, 2H); 7.22 (s, 2H). $^{13}C\{^1H\}$ NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.6; 16.5; 31.4; 35.3; 43.2; 64.6; 119.7; 125.9; 128.9; 139.5; 141.3; 145.2; 148.7;

162.3. For $C_{32}H_{44}O_2Si$, 488.79, Calc.: C 78.63% H 9.07% O 6.55%. Found: C 59.69% H 5.62% O 6.26%.

Preparation of [μ-(η^5-6-tert-butyl-5-methoxy-2-methylinden-4-yl)(η^5-fluoren-9-yl)dimethylsilylene] dichlorozirconium(IV) ***(13)****.* Manipulations were performed in Schlenck type vessels. *n*-BuLi (1.9 ml of 1.6 M hexane solution, 3 mmol) was dropwise added to a cold (-60 °C) solution of **9** (0.62 g, 1.41 mmol) in Et_2O (20 ml). The reaction mixture was allowed to warm to room temperature, cooled to -60 °C; a solution of $ZrCl_4$ (0.36 g, 1.52 mmol) in pentane (10 ml) was added to it. The mixture was allowed to warm to room temperature while stirring. After 16 h, the resulting precipitate was separated by decantation, washed with Et_2O/pentane, and recrystallized from a toluene-hexane (2:1) mixture. The yield was 0.16 g (19%), orange crystals. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.00 (s, 3H); 1.36 (s, 3H); 1.41 (s, 9H); 1.92 (s, 3H), 4.12 (s, 3H); 6.13 (bs, 1H); 6.45 (bs, 1H); 6.84 (d, *J* = 8.6 Hz, 1H); 6.96 (t, *J* = 7.7 Hz, 1H); 7.29 (s, 1H); 7.40 (t, *J* = 7.7 Hz, 2H); 7.60 (t, *J* = 8.1 Hz, 1H); 7.82 (d, *J* = 8.6 Hz, 1H); 7.94 (d, *J* = 8.4 Hz, 1H); 7.97 (d, *J* = 8.4 Hz, 1H). ^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$, 20 °C): δ = -0.13; 1.28; 16.9; 30.1; 35.6; 65.6; 88.5; 98.5; 107.3; 122.7; 123.1; 123.4; 124.3; 124.4; 125.6; 125.7; 126.1; 126.2; 126.7; 127.4; 128.0; 128.4; 128.5; 129.3; 139.7; 142.9; 165.0. For $C_{30}H_{31}Cl_2OSiZr$, 597.79, Calc.: C 60.28% H 5.23% O 2.68%. Found: C 59.40% H 5.40% O 2.55%.

Preparation of dichlorozirconium(IV) 7,7′-μ-dimethylsilylenebis(η^5-6-tert-Butyl-5-methoxy-2-methylinden-4-ide) ***(14)****.* Manipulations were performed in Schlenck type vessels. *n*-BuLi (1.07 ml of 2.5M hexane solution, 1.72 mmol) was dropwise added to a cold (-60 °C) solution of **10** (0.4 g, 0.82 mmol) in a Et_2O (15 ml) / pentane (10 ml) mixture. The reaction mixture was allowed to warm to room temperature, cooled to -60 °C. A solution of $ZrCl_4$ (0.21 g, 0.9 mmol) in pentane (10 ml) was added to it. The mixture was allowed to warm to room temperature while stirring. After 16 h, the resulting precipitate was separated by decantation, washed with pentane, and recrystallized from Et_2O. The yield of *rac*-form was 0.15 g (28%), pale yellow crystalline powder. For *rac*-form ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.01 (s, 6H); 1.43 (s, 18H); 2.02 (s, 6H); 3.90 (s, 6H); 4.03 (d, $^4J_{HH}$ = 2.2 Hz, 2H), 6.23 (d, $^4J_{HH}$ = 2.2 Hz, 2H), 7.56 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 20 °C): δ = -1.0; 16.9; 30.6; 35.8; 64.8; 104.8; 108.6; 122.7; 125.1; 127.2; 127.4; 140.3; 142.0; 166.7. For $C_{32}H_{42}Cl_2O_2SiZr$, 648.90, Calc.: C 59.23% H 6.52% O 4.93%. Found: C 58.44% H 6.66% O 4.81%.

Mother liquor contains mixture of *rac*- and *meso*-forms. For *meso*-form ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.21 (s, 6H); 1.36 (s, 6H); 1.41(s, 18H); 2.26 (s, 6H); 3.59 (s, 6H); 6.17 (br, 4H); 7.61 (s, 2H).

*Crystal structure determination of **14**.* A single yellow crystal of **14** with approximate dimensions 0.20 × 0.15 × 0.10 mm^3 was mounted using an inert oil in the hole of plastic CryoLoop and transferred to a cold air stream on the Bruker SMART APEX II diffractometer.

Crystal data: $C_{32}H_{42}Cl_2O_2Si_1Zr_1$, M = 648.87, monoclinic, a = 21.882(5), b = 10.523(2), c = 14.853(3) Å, β = 113.402(3)°, V = 3138.6(11) $Å^3$, space group $C2/c$, Z = 4, D_c = 1.373 g/cm^3, $F(000)$ = 1352, μ(Mo-Kα) = 0.586 mm^{-1}.

Data collection, structure solution and refinement. Total of 14726 reflections (3436 unique, R_{int} = 0.0330) were measured using graphite monochromatized Mo-Kα radiation (λ=0.71073 Å) at 173.0(2) K. Data were collected in the range 2.03 < θ < 27.00 (-27 ≤ h ≤ 27, -13 ≤ k ≤ 13, -18 ≤ 1 ≤ 18). Omega scan mode with the step of 0.5 deg (10 sec. per step) was used. Absorption correction based on measurements of equivalent reflections was applied. [1] The structure was solved by direct methods [2] and refined by full matrix least-squares on F^2 [3] with anisotropic thermal parameters for all non-hydrogen atoms. All H atoms were placed in calculated positions and refined using a riding model. The final residuals were: R_1 = 0.0299, wR_2 = 0.0765 for 2970 reflections with I>2σ(I) and 0.0370, 0.0796 for all data and 179 parameters. Goof = 1.052, maximum Δρ = 0.377 e/$Å^3$.

References

1. Sheldrick, G. M. *SADABS*, Program for scaling and correction of area detector data. University of Göttingen. Germany, 1997.
2. Sheldrick, G. M. *Acta. Crystallogr*., 2008, **A64**, 112.
3. Sheldrick, G. M. *Acta. Crystallogr*., 2015, **C71**, 3.

Table S1 Crystal data, data colection, structure solution and refinement parameters for **14.**

Empirical formula	C32 H42 Cl2 O2 Si Zr	
Formula weight	648.87	
Color, habit	colourless block	
Crystal size	0.20 x 0.15 x 0.10 mm^3	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 21.882(5) Å	α= 90°.
	b = 10.523(2) Å	β= 113.402(3)°.
	c = 14.853(3) Å	γ = 90°.
Volume	3138.6(11) $Å^3$	
Z	4	
Calculated density	1.373 g/cm^3	
Absorption coefficient	0.586 mm^{-1}	
F(000)	1352	
Theta range for data collection	2.03 to 27.00°.	
Index ranges	-27<=h<=27, -13<=k<=13, -18<=l<=18	
Reflections collected	14726	

Independent reflections	3436 [R(int) = 0.0330]
Completeness to theta = 27.00°	100.0 %
Absorption correction	Semi-empirical from equivalents (SADABS [1])
Max. and min. transmission	0.9438 and 0.8919
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3436 / 0 / 179
Goodness-of-fit on F^2	1.052
Final R indices [I>2sigma(I)]	R1 = 0.0299, wR2 = 0.0765
R indices (all data)	R1 = 0.0370, wR2 = 0.0796
Largest diff. peak and hole	0.377 and -0.397 e•Å^{-3}
Solution method	Direct methods (SHELXS [2])
Refinement method	Full-matrix least-squares on F^2 (SHELXL [3])
Hydrogen treatment	All H atoms were placed in calc. positions and refined using a riding model.
Data / restraints / parameters	3436 / 0 / 179

Table S2 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **14**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zr(1)	5000	6394(1)	7500	27(1)
Cl(1)	4184(1)	4871(1)	7563(1)	53(1)
Si(1)	5000	10589(1)	7500	25(1)
O(1)	3742(1)	10585(1)	8048(1)	31(1)
C(1)	5357(1)	6332(2)	9334(2)	35(1)
C(2)	5919(1)	6761(2)	9206(2)	33(1)
C(3)	5756(1)	7924(2)	8682(1)	27(1)
C(4)	5103(1)	8300(2)	8598(1)	23(1)
C(5)	4715(1)	9425(2)	8224(1)	22(1)
C(6)	4116(1)	9479(2)	8324(1)	24(1)
C(7)	3821(1)	8436(2)	8636(1)	28(1)
C(8)	4199(1)	7361(2)	8963(1)	30(1)
C(9)	4852(1)	7292(2)	8995(1)	27(1)
C(10)	6590(1)	6146(2)	9581(2)	48(1)
C(11)	5691(1)	11573(2)	8374(2)	41(1)
C(12)	4024(1)	11624(2)	8708(2)	40(1)
C(13)	3090(1)	8478(2)	8517(2)	38(1)
C(14)	2946(1)	9584(2)	9076(2)	51(1)
C(15)	2893(1)	7253(2)	8891(2)	59(1)
C(16)	2650(1)	8616(2)	7412(2)	54(1)

Table S3 Bond lengths [Å] for **14**.

Zr(1)-Cl(1)	2.4292(6)	C(2)-C(3)	1.418(2)	C(10)-H(10B)	0.9800
Zr(1)-C(3)	2.4707(19)	C(2)-C(10)	1.495(3)	C(10)-H(10C)	0.9800
Zr(1)-C(1)	2.519(2)	C(3)-C(4)	1.440(2)	C(11)-H(11A)	0.9800
Zr(1)-C(4)	2.5379(17)	C(3)-H(3)	0.9500	C(11)-H(11B)	0.9800
Zr(1)-C(9)	2.5486(18)	C(4)-C(9)	1.423(2)	C(11)-H(11C)	0.9800
Zr(1)-C(2)	2.563(2)	C(4)-C(5)	1.434(2)	C(12)-H(12A)	0.9800
Si(1)-C(11)	1.867(2)	C(5)-C(6)	1.378(2)	C(12)-H(12B)	0.9800
Si(1)-C(5)	1.8925(18)	C(6)-C(7)	1.439(3)	C(12)-H(12C)	0.9800
O(1)-C(6)	1.388(2)	C(7)-C(8)	1.371(3)	C(13)-C(15)	1.531(3)
O(1)-C(12)	1.434(2)	C(7)-C(13)	1.539(3)	C(13)-C(14)	1.533(3)
C(1)-C(2)	1.393(3)	C(8)-C(9)	1.414(2)	C(13)-C(16)	1.546(3)
C(1)-C(9)	1.432(3)	C(8)-H(8)	0.9500	C(14)-H(14A)	0.9800
C(1)-H(1)	0.9500	C(10)-H(10A)	0.9800	C(14)-H(14B)	0.9800

C(14)-H(14C)	0.9800	C(15)-H(15C)	0.9800	C(16)-H(16C)	0.9800
C(15)-H(15A)	0.9800	C(16)-H(16A)	0.9800		
C(15)-H(15B)	0.9800	C(16)-H(16B)	0.9800		

Table S4 Bond angles [deg] for **14**.

Cl(1)-Zr(1)-Cl(1)#1	97.39(3)	C(4)-Zr(1)-C(2)	53.91(6)	O(1)-C(6)-C(7)	116.63(16)
Cl(1)-Zr(1)-C(3)	134.23(4)	C(4)#1-Zr(1)-C(2)	110.56(6)	C(8)-C(7)-C(6)	117.30(17)
Cl(1)#1-Zr(1)-C(3)	99.36(5)	C(9)-Zr(1)-C(2)	53.41(6)	C(8)-C(7)-C(13)	121.16(17)
Cl(1)-Zr(1)-C(3)#1	99.36(5)	C(9)#1-Zr(1)-C(2)	118.98(6)	C(6)-C(7)-C(13)	121.30(16)
Cl(1)#1-Zr(1)-C(3)#1	134.23(4)	Cl(1)-Zr(1)-C(2)#1	80.64(5)	C(7)-C(8)-C(9)	120.93(17)
C(3)-Zr(1)-C(3)#1	98.67(8)	Cl(1)#1-Zr(1)-C(2)#1	111.19(5)	C(7)-C(8)-H(8)	119.5
Cl(1)-Zr(1)-C(1)	81.84(5)	C(3)-Zr(1)-C(2)#1	130.22(6)	C(9)-C(8)-H(8)	119.5
Cl(1)#1-Zr(1)-C(1)	96.18(5)	C(3)#1-Zr(1)-C(2)#1	32.66(6)	C(8)-C(9)-C(4)	119.88(16)
C(3)-Zr(1)-C(1)	54.26(6)	C(1)-Zr(1)-C(2)#1	149.07(6)	C(8)-C(9)-C(1)	132.52(17)
C(3)#1-Zr(1)-C(1)	128.17(6)	C(1)#1-Zr(1)-C(2)#1	31.79(6)	C(4)-C(9)-C(1)	107.55(16)
Cl(1)-Zr(1)-C(1)#1	96.18(5)	C(4)-Zr(1)-C(2)#1	110.56(6)	C(8)-C(9)-Zr(1)	117.79(13)
Cl(1)#1-Zr(1)-C(1)#1	81.84(5)	C(4)#1-Zr(1)-C(2)#1	53.91(6)	C(4)-C(9)-Zr(1)	73.33(10)
C(3)-Zr(1)-C(1)#1	128.17(6)	C(9)-Zr(1)-C(2)#1	118.98(6)	C(1)-C(9)-Zr(1)	72.47(11)
C(3)#1-Zr(1)-C(1)#1	54.26(6)	C(9)#1-Zr(1)-C(2)#1	53.41(6)	C(2)-C(10)-H(10A)	109.5
C(1)-Zr(1)-C(1)#1	177.03(9)	C(2)-Zr(1)-C(2)#1	162.69(9)	C(2)-C(10)-H(10B)	109.5
Cl(1)-Zr(1)-C(4)	112.05(4)	C(11)#1-Si(1)-C(11)	112.62(15)	H(10A)-C(10)-H(10B)	109.5
Cl(1)#1-Zr(1)-C(4)	131.87(4)	C(11)#1-Si(1)-C(5)	113.29(9)	C(2)-C(10)-H(10C)	109.5
C(3)-Zr(1)-C(4)	33.38(6)	C(11)-Si(1)-C(5)	108.84(8)	H(10A)-C(10)-H(10C)	109.5
C(3)#1-Zr(1)-C(4)	78.78(6)	C(11)#1-Si(1)-C(5)#1	108.84(8)	H(10B)-C(10)-H(10C)	109.5
C(1)-Zr(1)-C(4)	54.20(6)	C(11)-Si(1)-C(5)#1	113.29(9)	Si(1)-C(11)-H(11A)	109.5
C(1)#1-Zr(1)-C(4)	128.76(6)	C(5)-Si(1)-C(5)#1	99.31(10)	Si(1)-C(11)-H(11B)	109.5
Cl(1)-Zr(1)-C(4)#1	131.87(4)	C(6)-O(1)-C(12)	113.20(14)	H(11A)-C(11)-H(11B)	109.5
Cl(1)#1-Zr(1)-C(4)#1	112.05(4)	C(2)-C(1)-C(9)	108.82(16)	Si(1)-C(11)-H(11C)	109.5
C(3)-Zr(1)-C(4)#1	78.78(6)	C(2)-C(1)-Zr(1)	75.84(12)	H(11A)-C(11)-H(11C)	109.5
C(3)#1-Zr(1)-C(4)#1	33.38(6)	C(9)-C(1)-Zr(1)	74.71(11)	H(11B)-C(11)-H(11C)	109.5
C(1)-Zr(1)-C(4)#1	128.76(6)	C(2)-C(1)-H(1)	125.6	O(1)-C(12)-H(12A)	109.5
C(1)#1-Zr(1)-C(4)#1	54.20(6)	C(9)-C(1)-H(1)	125.6	O(1)-C(12)-H(12B)	109.5
C(4)-Zr(1)-C(4)#1	75.63(8)	Zr(1)-C(1)-H(1)	115.9	H(12A)-C(12)-H(12B)	109.5
Cl(1)-Zr(1)-C(9)	82.05(4)	C(1)-C(2)-C(3)	108.12(17)	O(1)-C(12)-H(12C)	109.5
Cl(1)#1-Zr(1)-C(9)	128.88(4)	C(1)-C(2)-C(10)	126.83(18)	H(12A)-C(12)-H(12C)	109.5
C(3)-Zr(1)-C(9)	54.55(6)	C(3)-C(2)-C(10)	125.02(18)	H(12B)-C(12)-H(12C)	109.5
C(3)#1-Zr(1)-C(9)	95.55(6)	C(1)-C(2)-Zr(1)	72.37(13)	C(15)-C(13)-C(14)	107.2(2)
C(1)-Zr(1)-C(9)	32.83(6)	C(3)-C(2)-Zr(1)	70.08(11)	C(15)-C(13)-C(7)	111.34(17)
C(1)#1-Zr(1)-C(9)	149.27(6)	C(10)-C(2)-Zr(1)	124.87(15)	C(14)-C(13)-C(7)	112.80(18)
C(4)-Zr(1)-C(9)	32.50(5)	C(2)-C(3)-C(4)	108.01(16)	C(15)-C(13)-C(16)	108.5(2)
C(4)#1-Zr(1)-C(9)	104.93(6)	C(2)-C(3)-Zr(1)	77.25(12)	C(14)-C(13)-C(16)	109.18(19)
Cl(1)-Zr(1)-C(9)#1	128.88(4)	C(4)-C(3)-Zr(1)	75.87(10)	C(7)-C(13)-C(16)	107.78(18)
Cl(1)#1-Zr(1)-C(9)#1	82.05(4)	C(2)-C(3)-H(3)	126.0	C(13)-C(14)-H(14A)	109.5
C(3)-Zr(1)-C(9)#1	95.55(6)	C(4)-C(3)-H(3)	126.0	C(13)-C(14)-H(14B)	109.5
C(3)#1-Zr(1)-C(9)#1	54.55(6)	Zr(1)-C(3)-H(3)	113.3	H(14A)-C(14)-H(14B)	109.5
C(1)-Zr(1)-C(9)#1	149.27(6)	C(9)-C(4)-C(5)	120.61(16)	C(13)-C(14)-H(14C)	109.5
C(1)#1-Zr(1)-C(9)#1	32.83(6)	C(9)-C(4)-C(3)	106.97(15)	H(14A)-C(14)-H(14C)	109.5
C(4)-Zr(1)-C(9)#1	104.93(6)	C(5)-C(4)-C(3)	132.42(16)	H(14B)-C(14)-H(14C)	109.5
C(4)#1-Zr(1)-C(9)#1	32.50(5)	C(9)-C(4)-Zr(1)	74.16(10)	C(13)-C(15)-H(15A)	109.5
C(9)-Zr(1)-C(9)#1	136.48(8)	C(5)-C(4)-Zr(1)	121.03(12)	C(13)-C(15)-H(15B)	109.5
Cl(1)-Zr(1)-C(2)	111.19(5)	C(3)-C(4)-Zr(1)	70.75(10)	H(15A)-C(15)-H(15B)	109.5
Cl(1)#1-Zr(1)-C(2)	80.64(5)	C(6)-C(5)-C(4)	115.77(15)	C(13)-C(15)-H(15C)	109.5
C(3)-Zr(1)-C(2)	32.66(6)	C(6)-C(5)-Si(1)	125.24(13)	H(15A)-C(15)-H(15C)	109.5
C(3)#1-Zr(1)-C(2)	130.22(6)	C(4)-C(5)-Si(1)	118.47(13)	H(15B)-C(15)-H(15C)	109.5
C(1)-Zr(1)-C(2)	31.79(6)	C(5)-C(6)-O(1)	118.50(16)	C(13)-C(16)-H(16A)	109.5
C(1)#1-Zr(1)-C(2)	149.07(6)	C(5)-C(6)-C(7)	124.74(16)	C(13)-C(16)-H(16B)	109.5

H(16A)-C(16)-H(16B)	109.5	H(16A)-C(16)-H(16C)	109.5
C(13)-C(16)-H(16C)	109.5	H(16B)-C(16)-H(16C)	109.5

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+3/2

Table S5 Anisotropic displacement parameters ($Å^2$ x 10^3) for **14**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zr(1)	36(1)	14(1)	42(1)	0	27(1)	0
Cl(1)	73(1)	28(1)	81(1)	-7(1)	54(1)	-20(1)
Si(1)	35(1)	15(1)	24(1)	0	11(1)	0
O(1)	33(1)	24(1)	34(1)	-1(1)	11(1)	11(1)
C(1)	44(1)	28(1)	45(1)	15(1)	30(1)	11(1)
C(2)	37(1)	31(1)	37(1)	12(1)	22(1)	13(1)
C(3)	30(1)	26(1)	29(1)	5(1)	16(1)	5(1)
C(4)	28(1)	21(1)	23(1)	0(1)	12(1)	3(1)
C(5)	28(1)	18(1)	22(1)	-2(1)	10(1)	3(1)
C(6)	30(1)	20(1)	22(1)	-2(1)	10(1)	5(1)
C(7)	30(1)	28(1)	31(1)	-5(1)	17(1)	1(1)
C(8)	37(1)	26(1)	37(1)	3(1)	25(1)	2(1)
C(9)	36(1)	23(1)	30(1)	5(1)	20(1)	5(1)
C(10)	42(1)	52(1)	58(2)	25(1)	29(1)	25(1)
C(11)	58(1)	31(1)	33(1)	-7(1)	17(1)	-16(1)
C(12)	47(1)	26(1)	48(1)	-8(1)	20(1)	10(1)
C(13)	30(1)	38(1)	51(1)	-2(1)	21(1)	3(1)
C(14)	47(1)	56(2)	61(2)	1(1)	35(1)	16(1)
C(15)	43(1)	53(2)	100(2)	6(1)	47(2)	-2(1)
C(16)	31(1)	65(2)	57(2)	-10(1)	8(1)	-4(1)

Table S6 Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **14**.

	x	y	z	U(eq)
H(1)	5315	5534	9603	42
H(3)	6030	8377	8430	32
H(8)	4019	6653	9171	36
H(10A)	6847	6417	10258	72
H(10B)	6826	6397	9169	72
H(10C)	6538	5220	9561	72
H(11A)	5768	12309	8027	61
H(11B)	6098	11061	8645	61
H(11C)	5571	11867	8908	61
H(12A)	3747	12383	8464	60
H(12B)	4475	11796	8750	60
H(12C)	4043	11405	9359	60
H(14A)	3286	9605	9748	76
H(14B)	2506	9468	9092	76
H(14C)	2955	10385	8746	76
H(15A)	3175	7142	9588	89
H(15B)	2953	6527	8520	89
H(15C)	2426	7305	8802	89
H(16A)	2182	8690	7318	81
H(16B)	2706	7866	7060	81
H(16C)	2782	9379	7156	81