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Dichloridobis{*N*-[(dimethylamino)dimethylsilyl]-2,6-dimethylanilido-$\kappa^2 N,N'$}zirconium(IV)

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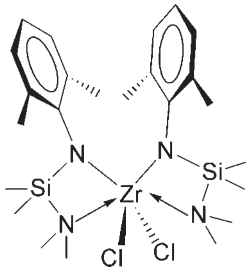
Key indicators: single-crystal X-ray study; T = 203 K; mean σ(C–C) = 0.006 Å; R factor = 0.048; wR factor = 0.120; data-to-parameter ratio = 16.9.

The monomeric title zirconium(IV) compound, $[Zr(C_{12}H_{21}N_2Si)_2Cl_2]$, was prepared by the metathetical reaction of $[LiN(SiMe_2NMe_2)(2,6\text{-}Me_2C_6H_3)]_2$ with zirconium tetrachloride. The Zr^{IV} atom is *N*,*N*′-chelated by the *N*-silylated anilido ligand. Along with two Cl atoms, the six-coordinated Zr^{IV} atom demonstrates a highly distorted octahedral geometry. The two ligands around the Zr^{IV} atom are arranged *cis* to each other and obey the C_2 symmetry operation. That means the asymmetric unit consists of only half of the molecular compound and the complete molecule is generated by a twofold axis. The two ends of the N—Si—N chelating unit exhibit different affinities for the metal center. The Zr—N$_{amino}$ bond is longer than the Zr—N$_{anilido}$ bond.

Related literature

For the catalytic applications of related *N*-silylated analido group 4 metal compounds towards olefin polymerization, see: Gibson *et al.* (1998); Hill & Hitchcock (2002). For related organometallic compounds supported with analogous analido ligands, see: Schumann *et al.* (2000); Chen *et al.* (2007); Ferreira *et al.* (2007); Chen (2008).



Experimental

Crystal data

$[Zr(C_{12}H_{21}N_2Si)_2Cl_2]$
M_r = 604.92
Monoclinic, $C2/c$
a = 16.179 (2) Å
b = 10.257 (2) Å
c = 18.779 (4) Å
β = 112.234 (4)°
V = 2884.6 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.67 mm^{-1}
T = 203 K
0.20 × 0.20 × 0.20 mm

Data collection

Bruker SMART area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.757, T_{max} = 0.878
6014 measured reflections
2548 independent reflections
2448 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.120
S = 1.20
2548 reflections
151 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.52 e Å^{-3}
$\Delta\rho_{min}$ = −0.53 e Å^{-3}

Table 1
Selected bond lengths (Å).

Zr1—N1	2.119 (3)	Zr1—Cl1	2.4676 (11)
Zr1—N2	2.439 (3)		

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL/PC* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: VM2005).

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supplementary materials

Acta Cryst. (2009). E**65**, m1307 [**doi:10.1107/S1600536809039804**]

Dichloridobis{*N*-[(dimethylamino)dimethylsilyl]-2,6-dimethylanilido-$\kappa^2 N,N'$}zirconium(IV)

J. Chen

Comment

Group 4 metal amides supported with the *N*-silylated anilido ligands were active catalysts for olefin polymerization (Gibson *et al.*, 1998; Hill & Hitchcock, 2002). The *N*-silylated anilido ligand in the title compound has a pendant amino group. It results in an N—Si—N chelating moiety, which is presumed to be a "quasi" conjugated unit owing to *d*–π interaction between Si and N atoms. The zinc compound coordinated with the analogous ligand has been reported by Schumann *et al.* (2000). The title compound is monomeric and contains two *N*-silylated anilido ligands, which give the N—Zr—N bite angle of 67.63° and are arranged *cis* to each other and obey the C_2 symmetrical operation. That means the asymmetric unit consists of only half of the molecular compound and the complete molecule is generated by a twofold axis. The Zr^{IV} atom is situated in the plane defined by atoms N1, N2A and Cl1, and the symmetrical counterparts. Both planes are perpendicular to each other resulting in a highly distorted octahedral geometry. Two ends of the N—Si—N chelating unit exhibit different affinity to the metal center. The $Zr—N_{anilido}$ bond is 2.119 Å and the $Zr—N_{amino}$ bond is 2.439 Å, suggesting the former is much tighter than the latter.

Experimental

$ZrCl_4$ (0.47 g, 2.03 mmol) was added into the solution of $[LiN(SiMe_2NMe_2)(2,6\text{-}Me_2C_6H_3)]_2$ (0.92 g, 2.03 mmol) in Et_2O (30 ml) at 273 K. The reaction mixture was warmed to room temperature and kept stirring for 12 h. It was dried in vacuum to remove all volatiles and the residue was extracted with CH_2Cl_2 (30 ml). Concentration of the filtrate under reduced pressure gave the title compound as colorless crystals (yield 0.92 g, 75%).

Refinement

The methyl H atoms were constrained to an ideal geometry, with C—H distances of 0.97 Å and $U_{iso}(H) = 1.5U_{eq}(C)$, but each group was allowed to rotate freely about its C–C, C–N and C–Si bonds. The other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances in the range 0.94Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Figures

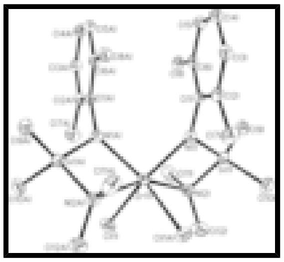


Fig. 1. The molecular structure, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Hydrogens omitted for clarity. Symmetry codes: (i) -*x*, *y*, -*z* + 1/2.

Dichloridobis{*N*-[(dimethylamino)dimethylsilyl]-2,6-dimethylanilido- κ^2N,N'}zirconium(IV)

Crystal data

$[Zr(C_{12}H_{21}N_2Si)_2Cl_2]$	$F(000) = 1264$
$M_r = 604.92$	$D_x = 1.393$ Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation, λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 3803 reflections
$a = 16.179$ (2) Å	θ = 2.3–27.1°
$b = 10.257$ (2) Å	$\mu = 0.67$ mm^{-1}
$c = 18.779$ (4) Å	$T = 203$ K
β = 112.234 (4)°	Block, colorless
$V = 2884.6$ (9) Å^3	0.20 × 0.20 × 0.20 mm
$Z = 4$	

Data collection

Bruker SMART area-detector diffractometer	2548 independent reflections
Radiation source: fine-focus sealed tube	2448 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.027$
φ and ω scans	$\theta_{max} = 25.0°$, $\theta_{min} = 2.3°$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$h = -19 \rightarrow 19$
$T_{min} = 0.757$, $T_{max} = 0.878$	$k = -12 \rightarrow 12$
6014 measured reflections	$l = -18 \rightarrow 22$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.048$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.120$	H-atom parameters constrained
$S = 1.20$	$w = 1/[\sigma^2(F_o^2) + (0.0465P)^2 + 9.9576P]$ where $P = (F_o^2 + 2F_c^2)/3$
2548 reflections	$(\Delta/\sigma)_{max} < 0.001$
151 parameters	$\Delta\rho_{max} = 0.52$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.53$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Zr1	0.0000	0.26497 (5)	0.2500	0.02462 (18)
Si1	−0.03902 (7)	0.19837 (11)	0.39184 (6)	0.0297 (3)
Cl1	−0.10371 (7)	0.42525 (10)	0.16362 (7)	0.0427 (3)
N1	0.01144 (19)	0.1249 (3)	0.33620 (17)	0.0249 (7)
N2	−0.0992 (2)	0.3112 (3)	0.3175 (2)	0.0337 (8)
C1	0.0574 (2)	0.0027 (3)	0.3583 (2)	0.0236 (8)
C2	0.1508 (2)	−0.0007 (4)	0.3993 (2)	0.0278 (8)
C3	0.1939 (3)	−0.1203 (4)	0.4175 (2)	0.0325 (9)
H3A	0.2562	−0.1222	0.4439	0.039*
C4	0.1478 (3)	−0.2359 (4)	0.3977 (2)	0.0345 (9)
H4A	0.1782	−0.3159	0.4099	0.041*
C5	0.0562 (3)	−0.2329 (4)	0.3598 (2)	0.0330 (9)
H5A	0.0245	−0.3118	0.3468	0.040*
C6	0.0100 (2)	−0.1158 (4)	0.3404 (2)	0.0265 (8)
C7	0.2058 (3)	0.1209 (4)	0.4260 (3)	0.0416 (11)
H7A	0.2680	0.0974	0.4527	0.062*
H7B	0.1851	0.1688	0.4607	0.062*
H7C	0.1998	0.1750	0.3820	0.062*
C8	−0.0900 (2)	−0.1221 (4)	0.3002 (2)	0.0314 (9)
H8A	−0.1059	−0.1936	0.2636	0.047*
H8B	−0.1118	−0.0409	0.2731	0.047*
H8C	−0.1169	−0.1360	0.3378	0.047*
C9	−0.1136 (3)	0.0973 (4)	0.4237 (3)	0.0404 (10)
H9A	−0.0987	0.1103	0.4783	0.061*
H9B	−0.1059	0.0061	0.4140	0.061*
H9C	−0.1752	0.1225	0.3955	0.061*
C10	0.0358 (3)	0.2854 (5)	0.4793 (3)	0.0458 (11)
H10A	0.0207	0.2609	0.5229	0.069*
H10B	0.0284	0.3787	0.4711	0.069*
H10C	0.0974	0.2618	0.4897	0.069*
C11	−0.1893 (3)	0.2614 (5)	0.2688 (3)	0.0478 (12)
H11A	−0.2305	0.2784	0.2941	0.072*
H11D	−0.1860	0.1683	0.2613	0.072*
H11C	−0.2100	0.3051	0.2194	0.072*
C12	−0.1088 (4)	0.4470 (5)	0.3400 (3)	0.0536 (13)
H12B	−0.1503	0.4492	0.3661	0.080*
H12C	−0.1312	0.5013	0.2944	0.080*
H12A	−0.0511	0.4794	0.3742	0.080*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zr1	0.0262 (3)	0.0198 (3)	0.0309 (3)	0.000	0.0142 (2)	0.000
Si1	0.0310 (6)	0.0305 (6)	0.0303 (6)	0.0019 (4)	0.0148 (5)	−0.0011 (4)
Cl1	0.0491 (6)	0.0310 (6)	0.0538 (7)	0.0120 (5)	0.0259 (6)	0.0139 (5)
N1	0.0206 (15)	0.0262 (17)	0.0273 (17)	0.0006 (12)	0.0086 (13)	−0.0026 (13)
N2	0.0347 (19)	0.0300 (19)	0.041 (2)	0.0072 (15)	0.0194 (16)	0.0046 (15)
C1	0.0258 (18)	0.0221 (19)	0.0225 (18)	0.0028 (15)	0.0086 (15)	−0.0003 (15)
C2	0.0254 (19)	0.033 (2)	0.025 (2)	−0.0016 (16)	0.0107 (16)	−0.0034 (16)
C3	0.028 (2)	0.043 (2)	0.026 (2)	0.0095 (18)	0.0101 (17)	0.0027 (18)
C4	0.040 (2)	0.032 (2)	0.033 (2)	0.0104 (18)	0.0139 (19)	0.0052 (18)
C5	0.041 (2)	0.026 (2)	0.033 (2)	−0.0030 (18)	0.0150 (19)	0.0014 (17)
C6	0.0272 (19)	0.032 (2)	0.0221 (19)	−0.0027 (16)	0.0113 (16)	−0.0016 (16)
C7	0.026 (2)	0.043 (3)	0.047 (3)	−0.0042 (19)	0.0039 (19)	−0.006 (2)
C8	0.028 (2)	0.035 (2)	0.032 (2)	−0.0067 (17)	0.0127 (18)	−0.0042 (17)
C9	0.047 (3)	0.042 (3)	0.041 (3)	0.002 (2)	0.027 (2)	0.002 (2)
C10	0.053 (3)	0.050 (3)	0.034 (2)	−0.005 (2)	0.017 (2)	−0.012 (2)
C11	0.031 (2)	0.060 (3)	0.052 (3)	0.009 (2)	0.016 (2)	0.019 (2)
C12	0.072 (3)	0.039 (3)	0.073 (4)	0.017 (2)	0.053 (3)	0.006 (2)

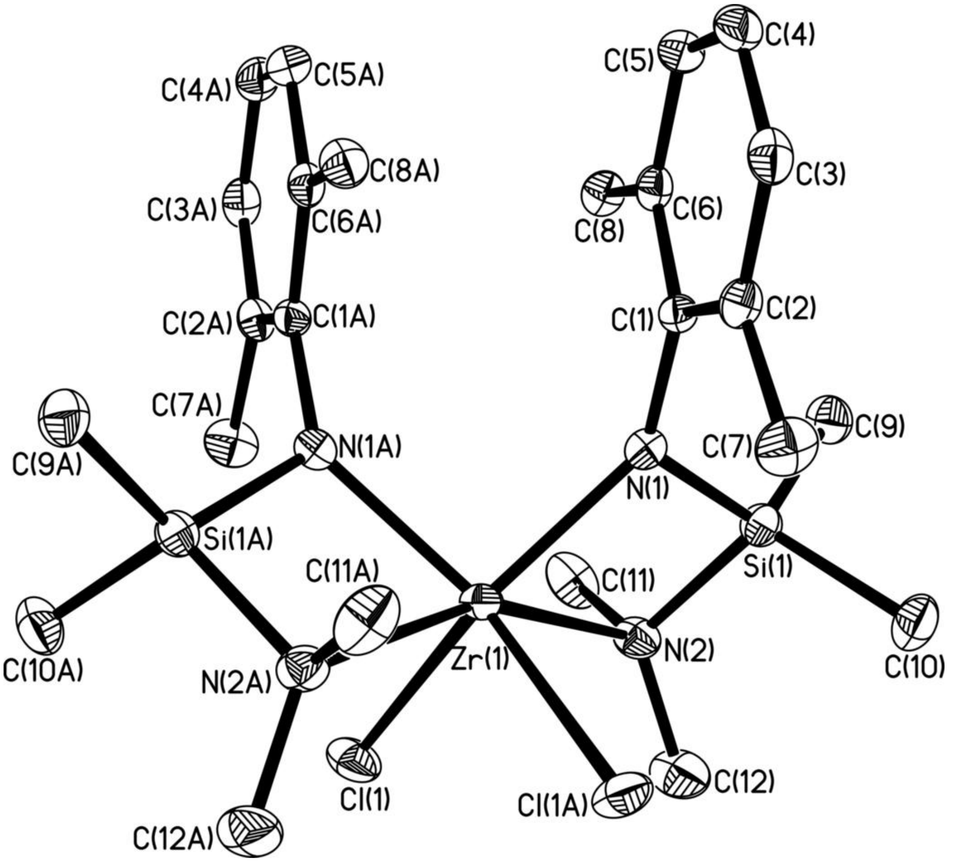
Geometric parameters (Å, °)

Zr1—N1^{i}	2.119 (3)	C5—C6	1.389 (6)
Zr1—N1	2.119 (3)	C5—H5A	0.9400
Zr1—N2^{i}	2.439 (3)	C6—C8	1.506 (5)
Zr1—N2	2.439 (3)	C7—H7A	0.9700
Zr1—Cl1^{i}	2.4676 (11)	C7—H7B	0.9700
Zr1—Cl1	2.4676 (11)	C7—H7C	0.9700
Zr1—Si1^{i}	3.0385 (12)	C8—H8A	0.9700
Si1—N1	1.724 (3)	C8—H8B	0.9700
Si1—N2	1.791 (4)	C8—H8C	0.9700
Si1—C9	1.854 (4)	C9—H9A	0.9700
Si1—C10	1.859 (5)	C9—H9B	0.9700
N1—C1	1.436 (5)	C9—H9C	0.9700
N2—C12	1.480 (6)	C10—H10A	0.9700
N2—C11	1.487 (6)	C10—H10B	0.9700
C1—C6	1.408 (5)	C10—H10C	0.9700
C1—C2	1.413 (5)	C11—H11A	0.9700
C2—C3	1.388 (6)	C11—H11D	0.9700
C2—C7	1.504 (6)	C11—H11C	0.9700
C3—C4	1.376 (6)	C12—H12B	0.9700
C3—H3A	0.9400	C12—H12C	0.9700
C4—C5	1.379 (6)	C12—H12A	0.9700
C4—H4A	0.9400		
N1^{i}—Zr1—N1	94.65 (16)	C3—C4—C5	119.2 (4)

N1^{i}—Zr1—N2^{i}	67.63 (11)	C3—C4—H4A	120.4
N1—Zr1—N2^{i}	130.12 (12)	C5—C4—H4A	120.4
N1^{i}—Zr1—N2	130.12 (12)	C4—C5—C6	121.4 (4)
N1—Zr1—N2	67.63 (11)	C4—C5—H5A	119.3
N2^{i}—Zr1—N2	157.56 (16)	C6—C5—H5A	119.3
N1^{i}—Zr1—Cl1^{i}	142.64 (8)	C5—C6—C1	119.5 (3)
N1—Zr1—Cl1^{i}	96.22 (9)	C5—C6—C8	117.7 (4)
N2^{i}—Zr1—Cl1^{i}	78.14 (8)	C1—C6—C8	122.8 (3)
N2—Zr1—Cl1^{i}	86.92 (9)	C2—C7—H7A	109.5
N1^{i}—Zr1—Cl1	96.22 (9)	C2—C7—H7B	109.5
N1—Zr1—Cl1	142.64 (8)	H7A—C7—H7B	109.5
N2^{i}—Zr1—Cl1	86.92 (9)	C2—C7—H7C	109.5
N2—Zr1—Cl1	78.14 (8)	H7A—C7—H7C	109.5
Cl1^{i}—Zr1—Cl1	96.45 (6)	H7B—C7—H7C	109.5
N1^{i}—Zr1—Si1^{i}	33.40 (8)	C6—C8—H8A	109.5
N1—Zr1—Si1^{i}	122.01 (9)	C6—C8—H8B	109.5
N2^{i}—Zr1—Si1^{i}	36.12 (8)	H8A—C8—H8B	109.5
N2—Zr1—Si1^{i}	153.54 (9)	C6—C8—H8C	109.5
Cl1^{i}—Zr1—Si1^{i}	114.26 (3)	H8A—C8—H8C	109.5
Cl1—Zr1—Si1^{i}	83.61 (4)	H8B—C8—H8C	109.5
N1—Si1—N2	93.02 (16)	Si1—C9—H9A	109.5
N1—Si1—C9	117.81 (19)	Si1—C9—H9B	109.5
N2—Si1—C9	112.64 (19)	H9A—C9—H9B	109.5
N1—Si1—C10	116.49 (19)	Si1—C9—H9C	109.5
N2—Si1—C10	111.0 (2)	H9A—C9—H9C	109.5
C9—Si1—C10	105.6 (2)	H9B—C9—H9C	109.5
C1—N1—Si1	121.2 (2)	Si1—C10—H10A	109.5
C1—N1—Zr1	134.3 (2)	Si1—C10—H10B	109.5
Si1—N1—Zr1	104.01 (15)	H10A—C10—H10B	109.5
C12—N2—C11	108.4 (4)	Si1—C10—H10C	109.5
C12—N2—Si1	118.1 (3)	H10A—C10—H10C	109.5
C11—N2—Si1	112.0 (3)	H10B—C10—H10C	109.5
C12—N2—Zr1	119.4 (3)	N2—C11—H11A	109.5
C11—N2—Zr1	107.3 (3)	N2—C11—H11D	109.5
Si1—N2—Zr1	90.49 (13)	H11A—C11—H11D	109.5
C6—C1—C2	118.9 (3)	N2—C11—H11C	109.5
C6—C1—N1	120.6 (3)	H11A—C11—H11C	109.5
C2—C1—N1	120.6 (3)	H11D—C11—H11C	109.5
C3—C2—C1	119.4 (4)	N2—C12—H12B	109.5
C3—C2—C7	118.1 (3)	N2—C12—H12C	109.5
C1—C2—C7	122.5 (3)	H12B—C12—H12C	109.5
C4—C3—C2	121.6 (4)	N2—C12—H12A	109.5
C4—C3—H3A	119.2	H12B—C12—H12A	109.5
C2—C3—H3A	119.2	H12C—C12—H12A	109.5

Symmetry codes: (i) $-x$, y, $-z+1/2$.

Fig. 1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C(8A)
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C(1A)
C(7A)
N(1A)
C(9A)
Si(1A)
C(11A)
C(10A)
N(2A)
Zr(1)
Cl(1)
C(12A)
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