# metal-organic compounds

# {N,N-Bis[2-(trimethylsilylamino)ethyl]-N′-(trimethylsilyl)ethane-1,2-diaminato(3−)-κ⁴N}methylzirconium(IV)

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The title compound, $[Zr(CH_3)(C_{15}H_{39}N_4Si_3)]$, is a unique example of a triamidoamine-supported zirconium–methyl complex that crystallized as a monomer with trigonal–bipyramidal geometry at zirconium, featuring a Zr—C bond of 2.2963 (16) Å.

## Related literature

For recent applications of $(N_3N)ZrMe$ in catalysis, see: Waterman (2007); Roering et al. (2007, 2008). For examples of structurally characterized triamidoamine-supported zirconium complexes, see: Duan et al. (1995); Morton et al. (1999, 2000); MacMillan et al. (2007). For related literature, see: Addison et al. (1984); Parkin (1992).
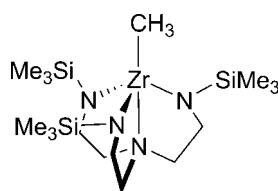


## Experimental

### Crystal data

$[Zr(CH_3)(C_{15}H_{39}N_4Si_3)]$
$M_r = 466.03$

Orthorhombic, $Pbca$
$a = 15.6018$ (7) Å

$b = 18.0682$ (8) Å
$c = 18.3745$ (8) Å
$V = 5179.7$ (4) Å³
$Z = 8$

Mo $K\alpha$ radiation
$\mu = 0.57$ mm⁻¹
$T = 125$ (2) K
$0.24 \times 0.20 \times 0.16$ mm

### Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 1999)
$T_{min} = 0.875$, $T_{max} = 0.914$

68275 measured reflections
6973 independent reflections
5714 reflections with $I > 2\sigma(I)$
$R_{int} = 0.033$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.063$
$S = 1.04$
6973 reflections

226 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.37$ e Å⁻³
$\Delta\rho_{min} = -0.29$ e Å⁻³

Data collection: SMART (Bruker, 2001); cell refinement: SAINT-Plus (Bruker, 1999); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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# supporting information

# {*N*,*N*-Bis[2-(trimethylsilylamino)ethyl]-*N′*-(trimethylsilyl)ethane-1,2-diaminato(3–)-*κ⁴N*}methylzirconium(IV)

## Samantha N. MacMillan, Joseph M. Tanski and Rory Waterman

### S1. Comment

Simple derivatives of triamidoamine-supported zirconium have recently been prepared, and these complexes have been found to be effective pre-catalysts for dehydrocoupling involving phosphines (Roering *et al.*, 2007; Waterman, 2007) and arsines (Roering *et al.*, 2008). Reaction of ($N_3N$)ZrCl with MeLi in $Et_2O$ afforded ($N_3N$)ZrMe (**I**, $N_3N$ = $N(CH_2CH_2NSiMe_3)_3{}^{3-}$)) in 82% yield as colorless crystals (Waterman, 2007). Complex **I** is highly lipophilic and exhibits reasonable thermal stability despite a low melting temperature (Mp = 87–91°C). Upon heating in benzene solution, methane is evolved, and the triamidolamine ligand is metalated at the trimethylsilyl functionality—a key step in dehydro-coupling catalysis (Waterman, 2007). Whereas zirconium complexes with methyl ligands are commonplace, those supported by triamidoamine ligands were previously unknown.

Complex **I** was crystallized from cold pentane solution and exhibits distorted trigonal bipyramidal geometry at zirconium. The $\tau5$-parameter for the complex was calculated as 1.1 (Addison *et al.*, 1984), though greater than 1, it is consistent with a trigonal bipyramidal geometry rather than square-pyramidal. The value greater than unity is attributed to the fact that the amido nitrogen atoms are not co-planar with Zr as expected for a trigonal pyramid, a feature that artificially increases the $\alpha$ angle in the $\tau5$-parameter calculation.

The three amido ligands orient in a roughly $C_3$-symmetric fashion about the Zr–C bonding axis with an average Zr—N bond length of 2.0714 (13) Å. The bond to the axial nitrogen appears to be effected by the relatively strong *trans*-directing methide ligand with Zr—N(4) = 2.538 (1) Å. This bond length is slightly longer than that observed for ($N_3N$)Zr(PHPh) with Zr—N(4) = 2.526 (2) Å (Roering *et al.* 2007) and considerably longer than that seen for arsenido derivatives ($N_3N$)ZrAsPh$_2$, Zr—N(4) = 2.516 (2) Å, and ($N_3N$)ZrAsHMes, Zr—N(4) = 2.502 (2) Å (Roering *et al.*, 2008).

For the methide ligand, the Zr—C bond length (2.2963 (16) Å) of **I** is slightly shorter than the most closely related complex structurally characterized complex ($N_3N*$)ZrCH$_2$Ph ($N_3N*$ = $N(CH_2CH_2NSiMe_2{}^tBu)_3{}^{3-}$), which displays Zr—C 2.3243 (18) Å (Morton *et al.*, 1999). Of the *ca* 315 complexes featuring a Zr—CH$_3$ bond, the Zr—C bond of **I** fits neatly into the range of reported Zr—C bond lengths of 2.046 to 2.805 Å.

The Hirshfeld Test Difference for Zr—C(16) is 6.71 su. This value is most likely the result of a small amount of contamination by the ($N_3N$)ZrCl precursor. This is an interesting observation given the high analytical purity of **I** and the inability to observe any ($N_3N$)ZrCl in benzene-$d_6$ solutions of **I** by $^1$H NMR spectroscopy. However, residual electron density was observed along the Zr—C vector, but this peak could not be refined as a chloride disorder. Contamination of crystals by trace quantities of chloride derivatives is known, and due caution must be taken in evaluating data (Parkin, 1992). While this test does not significantly detract from the quality of this structure and solution and correlation between the structure and spectroscopic assignment, it does indicate that contamination of product complexes with ($N_3N$)ZrCl is possible. This observation suggests that synthetic strategies for ($N_3N$)ZrX derivatives that circumvent the use of

(N₃N)ZrCl are optimal for achieving highly pure compounds for catalytic applications.

## S2. Experimental

Methyl complex (N₃N)ZrMe (**I**) was prepared according to the literature procedure (Waterman, 2007). Dissolving complex **I** (*ca* 800 mg) in minimal pentane (2 ml), then filtering and cooling the resulting colorless solution to -30 °C for extended periods (*ca* 1–2 weeks) afforded colorless, X-ray quality crystals.

## S3. Refinement

Hydrogen atoms on carbon were included in calculated positions and were refined using a riding model [C—H = 0.98 (CH₃), 0.99 Å (CH₂); $U_{iso} = 1.5\ U_{eq}$ (CH₃), $1.2\ U_{eq}$ (CH₂)]. The Hirshfeld test difference value Zr—C(16) = 6.71 su indicates slight contamination with the chloro precursor. The slighly low $U_{eq}$ value for Si(1) is likely the result of the terminal the atom residing in a trimethylsilyl substituent.
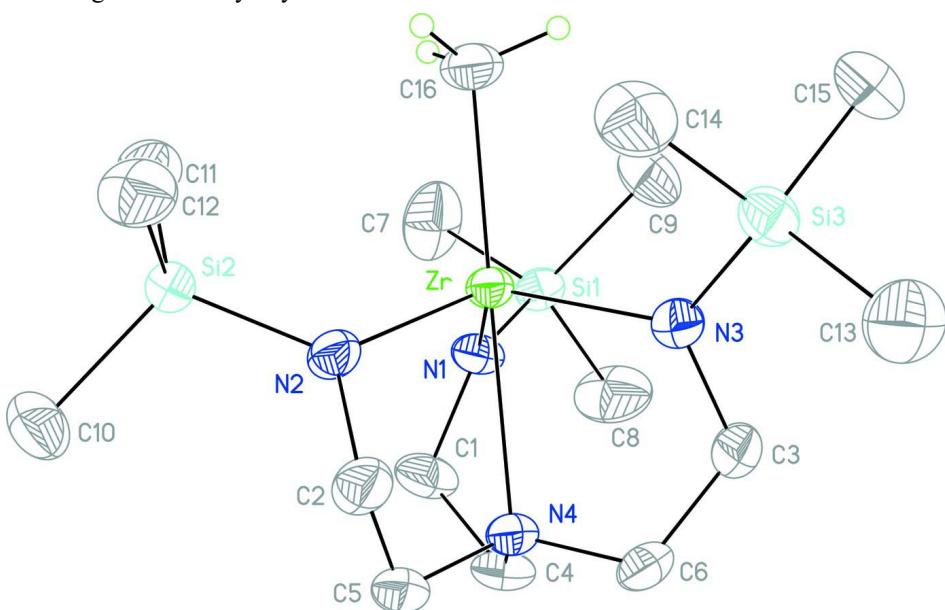


**Figure 1**

A view of complex **I**, with displacement ellipsoids shown at the 50% probability level. H atoms except those on C(16)have been omitted for clarity.

**{*N*,*N*-Bis[2-(trimethylsilylamino)ethyl]-*N′*-(trimethylsilyl)ethane-1,2- diaminato(3-)-*κ⁴N*}methylzirconium(IV)**

*Crystal data*

| | |
|---|---|
| [Zr(CH₃)(C₁₅H₃₉N₄Si₃)] | $D_x = 1.195$ Mg m⁻³ |
| $M_r = 466.03$ | Melting point: 362 K |
| Orthorhombic, *Pbca* | Mo *Kα* radiation, $\lambda = 0.71073$ Å |
| Hall symbol: -P 2ac 2ab | Cell parameters from 9832 reflections |
| $a = 15.6018\ (7)$ Å | $\theta = 2.5$–30.2° |
| $b = 18.0682\ (8)$ Å | $\mu = 0.57$ mm⁻¹ |
| $c = 18.3745\ (8)$ Å | $T = 125$ K |
| $V = 5179.7\ (4)$ Å³ | Block, colorless |
| $Z = 8$ | $0.24 \times 0.20 \times 0.16$ mm |
| $F(000) = 1984$ | |

*Data collection*

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 68275 measured reflections |
| Radiation source: fine-focus sealed tube | 6973 independent reflections |
| Graphite monochromator | 5714 reflections with $I > 2\sigma(I)$ |
| $\varphi$ and $\omega$ scans | $R_{int} = 0.033$ |
| Absorption correction: multi-scan ($SADABS$; Bruker, 1999) | $\theta_{max} = 29.1°$, $\theta_{min} = 2.1°$ |
| $T_{min} = 0.875$, $T_{max} = 0.914$ | $h = -21 \rightarrow 21$ |
| | $k = -24 \rightarrow 24$ |
| | $l = -24 \rightarrow 25$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.025$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.063$ | |
| $S = 1.04$ | H-atom parameters constrained |
| 6973 reflections | $w = 1/[\sigma^2(F_o^2) + (0.0241P)^2 + 2.7021P]$ |
| 226 parameters | where $P = (F_o^2 + 2F_c^2)/3$ |
| 0 restraints | $(\Delta/\sigma)_{max} = 0.002$ |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{max} = 0.37$ e Å$^{-3}$ |
| | $\Delta\rho_{min} = -0.29$ 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. EXTI refined to 0 and was removed from the refinement.

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

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Zr | 0.628126 (8) | 0.214931 (8) | 0.623919 (7) | 0.02366 (4) |
| N1 | 0.62324 (8) | 0.32650 (7) | 0.59830 (7) | 0.0296 (3) |
| N2 | 0.67984 (8) | 0.15023 (7) | 0.54191 (7) | 0.0302 (3) |
| N3 | 0.68857 (8) | 0.19705 (7) | 0.72277 (7) | 0.0293 (3) |
| N4 | 0.78205 (8) | 0.25715 (8) | 0.60724 (7) | 0.0294 (3) |
| Si1 | 0.55541 (3) | 0.39089 (2) | 0.63723 (2) | 0.02935 (9) |
| Si2 | 0.63047 (3) | 0.11014 (2) | 0.46778 (2) | 0.02709 (9) |
| Si3 | 0.66444 (3) | 0.12547 (3) | 0.78173 (3) | 0.03368 (10) |
| C1 | 0.69404 (11) | 0.35295 (10) | 0.55145 (10) | 0.0402 (4) |
| H1A | 0.6881 | 0.4068 | 0.5428 | 0.048* |
| H1B | 0.6922 | 0.3273 | 0.5039 | 0.048* |
| C2 | 0.77345 (10) | 0.13734 (10) | 0.54823 (10) | 0.0377 (4) |
| H2A | 0.7937 | 0.1066 | 0.5071 | 0.045* |
| H2B | 0.7864 | 0.1110 | 0.5942 | 0.045* |
| C3 | 0.76119 (10) | 0.24758 (10) | 0.73870 (9) | 0.0343 (3) |

| | | | |
|---|---|---|---|
| H3A | 0.7885 | 0.2335 | 0.7853 | 0.041* |
| H3B | 0.7402 | 0.2991 | 0.7430 | 0.041* |
| C4 | 0.77852 (10) | 0.33693 (9) | 0.58941 (10) | 0.0376 (4) |
| H4A | 0.8270 | 0.3503 | 0.5572 | 0.045* |
| H4B | 0.7830 | 0.3667 | 0.6345 | 0.045* |
| C5 | 0.81823 (10) | 0.21178 (10) | 0.54734 (9) | 0.0380 (4) |
| H5A | 0.8807 | 0.2051 | 0.5544 | 0.046* |
| H5B | 0.8088 | 0.2367 | 0.5000 | 0.046* |
| C6 | 0.82595 (10) | 0.24200 (10) | 0.67714 (9) | 0.0348 (4) |
| H6A | 0.8726 | 0.2783 | 0.6847 | 0.042* |
| H6B | 0.8514 | 0.1918 | 0.6762 | 0.042* |
| C7 | 0.46795 (15) | 0.41750 (14) | 0.57399 (13) | 0.0659 (7) |
| H7A | 0.4927 | 0.4371 | 0.5289 | 0.099* |
| H7B | 0.4321 | 0.4555 | 0.5968 | 0.099* |
| H7C | 0.4329 | 0.3739 | 0.5628 | 0.099* |
| C8 | 0.61459 (15) | 0.47570 (12) | 0.66494 (16) | 0.0670 (7) |
| H8A | 0.6359 | 0.5012 | 0.6215 | 0.101* |
| H8B | 0.6630 | 0.4619 | 0.6961 | 0.101* |
| H8C | 0.5760 | 0.5086 | 0.6918 | 0.101* |
| C9 | 0.50645 (14) | 0.35016 (11) | 0.72057 (10) | 0.0486 (5) |
| H9A | 0.4616 | 0.3149 | 0.7066 | 0.073* |
| H9B | 0.4813 | 0.3897 | 0.7502 | 0.073* |
| H9C | 0.5507 | 0.3245 | 0.7488 | 0.073* |
| C10 | 0.69439 (13) | 0.12628 (12) | 0.38323 (9) | 0.0491 (5) |
| H10A | 0.7510 | 0.1034 | 0.3885 | 0.074* |
| H10B | 0.7011 | 0.1796 | 0.3754 | 0.074* |
| H10C | 0.6646 | 0.1043 | 0.3415 | 0.074* |
| C11 | 0.52293 (11) | 0.15334 (11) | 0.45402 (10) | 0.0430 (4) |
| H11A | 0.4847 | 0.1388 | 0.4939 | 0.064* |
| H11B | 0.4988 | 0.1365 | 0.4076 | 0.064* |
| H11C | 0.5288 | 0.2073 | 0.4533 | 0.064* |
| C12 | 0.62003 (13) | 0.00839 (10) | 0.48219 (12) | 0.0458 (4) |
| H12A | 0.6771 | −0.0134 | 0.4883 | 0.069* |
| H12B | 0.5917 | −0.0140 | 0.4400 | 0.069* |
| H12C | 0.5858 | −0.0009 | 0.5259 | 0.069* |
| C13 | 0.76108 (14) | 0.09490 (13) | 0.83365 (13) | 0.0587 (6) |
| H13A | 0.8074 | 0.0831 | 0.7996 | 0.088* |
| H13B | 0.7469 | 0.0508 | 0.8623 | 0.088* |
| H13C | 0.7796 | 0.1347 | 0.8663 | 0.088* |
| C14 | 0.62506 (14) | 0.04485 (11) | 0.72743 (12) | 0.0524 (5) |
| H14A | 0.6661 | 0.0338 | 0.6885 | 0.079* |
| H14B | 0.5692 | 0.0569 | 0.7061 | 0.079* |
| H14C | 0.6192 | 0.0016 | 0.7592 | 0.079* |
| C15 | 0.58017 (14) | 0.15179 (12) | 0.84950 (11) | 0.0493 (5) |
| H15A | 0.6006 | 0.1935 | 0.8788 | 0.074* |
| H15B | 0.5682 | 0.1095 | 0.8813 | 0.074* |
| H15C | 0.5277 | 0.1661 | 0.8238 | 0.074* |
| C16 | 0.48882 (11) | 0.17738 (10) | 0.64014 (10) | 0.0399 (4) |

| | | | |
|---|---|---|---|
| H16A | 0.4821 | 0.1268 | 0.6219 | 0.060* |
| H16B | 0.4504 | 0.2106 | 0.6134 | 0.060* |
| H16C | 0.4746 | 0.1788 | 0.6921 | 0.060* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Zr | 0.01895 (7) | 0.02612 (7) | 0.02593 (7) | −0.00195 (5) | 0.00175 (5) | −0.00244 (5) |
| N1 | 0.0233 (6) | 0.0322 (7) | 0.0333 (6) | −0.0023 (5) | 0.0047 (5) | 0.0056 (5) |
| N2 | 0.0207 (6) | 0.0368 (7) | 0.0331 (7) | 0.0001 (5) | −0.0010 (5) | −0.0091 (6) |
| N3 | 0.0277 (6) | 0.0310 (6) | 0.0293 (6) | −0.0040 (5) | −0.0004 (5) | 0.0010 (5) |
| N4 | 0.0201 (6) | 0.0367 (7) | 0.0314 (6) | −0.0039 (5) | 0.0022 (5) | −0.0038 (5) |
| Si1 | 0.0265 (2) | 0.0259 (2) | 0.0356 (2) | −0.00213 (16) | −0.00132 (17) | 0.00063 (17) |
| Si2 | 0.02662 (19) | 0.0296 (2) | 0.02508 (19) | −0.00250 (16) | −0.00016 (16) | −0.00074 (16) |
| Si3 | 0.0355 (2) | 0.0320 (2) | 0.0335 (2) | 0.00130 (18) | 0.00282 (19) | 0.00533 (18) |
| C1 | 0.0315 (8) | 0.0440 (9) | 0.0450 (10) | −0.0025 (7) | 0.0093 (7) | 0.0153 (8) |
| C2 | 0.0243 (7) | 0.0475 (10) | 0.0412 (9) | 0.0053 (7) | −0.0011 (6) | −0.0145 (8) |
| C3 | 0.0352 (8) | 0.0383 (8) | 0.0295 (8) | −0.0074 (7) | −0.0037 (6) | −0.0029 (7) |
| C4 | 0.0264 (8) | 0.0383 (9) | 0.0482 (10) | −0.0090 (7) | 0.0090 (7) | 0.0055 (8) |
| C5 | 0.0206 (7) | 0.0563 (11) | 0.0372 (9) | −0.0022 (7) | 0.0053 (6) | −0.0089 (8) |
| C6 | 0.0233 (7) | 0.0430 (9) | 0.0380 (9) | −0.0065 (7) | −0.0058 (6) | −0.0052 (7) |
| C7 | 0.0610 (14) | 0.0767 (16) | 0.0600 (13) | 0.0338 (12) | −0.0199 (11) | −0.0094 (12) |
| C8 | 0.0627 (14) | 0.0414 (11) | 0.0969 (19) | −0.0193 (10) | 0.0106 (13) | −0.0183 (12) |
| C9 | 0.0580 (12) | 0.0409 (10) | 0.0470 (11) | 0.0056 (9) | 0.0205 (9) | −0.0002 (8) |
| C10 | 0.0489 (11) | 0.0676 (13) | 0.0307 (9) | −0.0012 (10) | 0.0073 (8) | 0.0052 (9) |
| C11 | 0.0326 (9) | 0.0530 (11) | 0.0433 (10) | 0.0031 (8) | −0.0063 (7) | 0.0083 (8) |
| C12 | 0.0477 (11) | 0.0303 (8) | 0.0595 (12) | −0.0051 (8) | 0.0075 (9) | −0.0054 (8) |
| C13 | 0.0523 (12) | 0.0595 (13) | 0.0644 (13) | 0.0087 (10) | −0.0095 (10) | 0.0215 (11) |
| C14 | 0.0650 (13) | 0.0348 (9) | 0.0573 (12) | −0.0100 (9) | 0.0060 (10) | 0.0016 (9) |
| C15 | 0.0521 (12) | 0.0534 (11) | 0.0425 (10) | 0.0007 (9) | 0.0142 (9) | 0.0079 (9) |
| C16 | 0.0290 (8) | 0.0441 (10) | 0.0465 (10) | −0.0095 (7) | 0.0061 (7) | −0.0078 (8) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Zr—N2 | 2.0709 (12) | C5—H5A | 0.9900 |
| Zr—N1 | 2.0715 (13) | C5—H5B | 0.9900 |
| Zr—N3 | 2.0719 (13) | C6—H6A | 0.9900 |
| Zr—C16 | 2.2963 (16) | C6—H6B | 0.9900 |
| Zr—N4 | 2.5383 (12) | C7—H7A | 0.9800 |
| N1—C1 | 1.4796 (19) | C7—H7B | 0.9800 |
| N1—Si1 | 1.7278 (14) | C7—H7C | 0.9800 |
| N2—C2 | 1.4834 (19) | C8—H8A | 0.9800 |
| N2—Si2 | 1.7242 (13) | C8—H8B | 0.9800 |
| N3—C3 | 1.484 (2) | C8—H8C | 0.9800 |
| N3—Si3 | 1.7286 (13) | C9—H9A | 0.9800 |
| N4—C4 | 1.479 (2) | C9—H9B | 0.9800 |
| N4—C6 | 1.481 (2) | C9—H9C | 0.9800 |
| N4—C5 | 1.484 (2) | C10—H10A | 0.9800 |

| | | | |
|---|---|---|---|
| Si1—C7 | 1.856 (2) | C10—H10B | 0.9800 |
| Si1—C8 | 1.860 (2) | C10—H10C | 0.9800 |
| Si1—C9 | 1.8628 (18) | C11—H11A | 0.9800 |
| Si2—C12 | 1.8646 (18) | C11—H11B | 0.9800 |
| Si2—C11 | 1.8678 (17) | C11—H11C | 0.9800 |
| Si2—C10 | 1.8690 (18) | C12—H12A | 0.9800 |
| Si3—C13 | 1.868 (2) | C12—H12B | 0.9800 |
| Si3—C14 | 1.870 (2) | C12—H12C | 0.9800 |
| Si3—C15 | 1.8723 (19) | C13—H13A | 0.9800 |
| C1—C4 | 1.519 (2) | C13—H13B | 0.9800 |
| C1—H1A | 0.9900 | C13—H13C | 0.9800 |
| C1—H1B | 0.9900 | C14—H14A | 0.9800 |
| C2—C5 | 1.516 (2) | C14—H14B | 0.9800 |
| C2—H2A | 0.9900 | C14—H14C | 0.9800 |
| C2—H2B | 0.9900 | C15—H15A | 0.9800 |
| C3—C6 | 1.520 (2) | C15—H15B | 0.9800 |
| C3—H3A | 0.9900 | C15—H15C | 0.9800 |
| C3—H3B | 0.9900 | C16—H16A | 0.9800 |
| C4—H4A | 0.9900 | C16—H16B | 0.9800 |
| C4—H4B | 0.9900 | C16—H16C | 0.9800 |
| | | | |
| N2—Zr—N1 | 113.48 (5) | N4—C5—H5B | 110.1 |
| N2—Zr—N3 | 111.87 (5) | C2—C5—H5B | 110.1 |
| N1—Zr—N3 | 111.57 (5) | H5A—C5—H5B | 108.4 |
| N2—Zr—C16 | 107.24 (6) | N4—C6—C3 | 109.00 (13) |
| N1—Zr—C16 | 106.40 (6) | N4—C6—H6A | 109.9 |
| N3—Zr—C16 | 105.72 (6) | C3—C6—H6A | 109.9 |
| N2—Zr—N4 | 73.33 (5) | N4—C6—H6B | 109.9 |
| N1—Zr—N4 | 73.43 (5) | C3—C6—H6B | 109.9 |
| N3—Zr—N4 | 73.86 (5) | H6A—C6—H6B | 108.3 |
| C16—Zr—N4 | 179.41 (5) | Si1—C7—H7A | 109.5 |
| C1—N1—Si1 | 118.72 (11) | Si1—C7—H7B | 109.5 |
| C1—N1—Zr | 114.78 (10) | H7A—C7—H7B | 109.5 |
| Si1—N1—Zr | 125.71 (7) | Si1—C7—H7C | 109.5 |
| C2—N2—Si2 | 115.83 (10) | H7A—C7—H7C | 109.5 |
| C2—N2—Zr | 114.53 (10) | H7B—C7—H7C | 109.5 |
| Si2—N2—Zr | 129.64 (7) | Si1—C8—H8A | 109.5 |
| C3—N3—Si3 | 120.19 (10) | Si1—C8—H8B | 109.5 |
| C3—N3—Zr | 115.11 (10) | H8A—C8—H8B | 109.5 |
| Si3—N3—Zr | 124.54 (7) | Si1—C8—H8C | 109.5 |
| C4—N4—C6 | 112.92 (13) | H8A—C8—H8C | 109.5 |
| C4—N4—C5 | 112.84 (13) | H8B—C8—H8C | 109.5 |
| C6—N4—C5 | 111.41 (13) | Si1—C9—H9A | 109.5 |
| C4—N4—Zr | 106.52 (9) | Si1—C9—H9B | 109.5 |
| C6—N4—Zr | 106.10 (9) | H9A—C9—H9B | 109.5 |
| C5—N4—Zr | 106.46 (9) | Si1—C9—H9C | 109.5 |
| N1—Si1—C7 | 111.45 (9) | H9A—C9—H9C | 109.5 |
| N1—Si1—C8 | 111.34 (9) | H9B—C9—H9C | 109.5 |

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| C7—Si1—C8 | 108.85 (12) | Si2—C10—H10A | 109.5 |
| N1—Si1—C9 | 108.99 (8) | Si2—C10—H10B | 109.5 |
| C7—Si1—C9 | 108.40 (11) | H10A—C10—H10B | 109.5 |
| C8—Si1—C9 | 107.70 (11) | Si2—C10—H10C | 109.5 |
| N2—Si2—C12 | 109.94 (8) | H10A—C10—H10C | 109.5 |
| N2—Si2—C11 | 109.44 (8) | H10B—C10—H10C | 109.5 |
| C12—Si2—C11 | 110.65 (9) | Si2—C11—H11A | 109.5 |
| N2—Si2—C10 | 110.66 (8) | Si2—C11—H11B | 109.5 |
| C12—Si2—C10 | 108.57 (10) | H11A—C11—H11B | 109.5 |
| C11—Si2—C10 | 107.55 (9) | Si2—C11—H11C | 109.5 |
| N3—Si3—C13 | 111.45 (9) | H11A—C11—H11C | 109.5 |
| N3—Si3—C14 | 108.66 (8) | H11B—C11—H11C | 109.5 |
| C13—Si3—C14 | 107.91 (11) | Si2—C12—H12A | 109.5 |
| N3—Si3—C15 | 112.32 (8) | Si2—C12—H12B | 109.5 |
| C13—Si3—C15 | 107.59 (10) | H12A—C12—H12B | 109.5 |
| C14—Si3—C15 | 108.79 (10) | Si2—C12—H12C | 109.5 |
| N1—C1—C4 | 108.61 (13) | H12A—C12—H12C | 109.5 |
| N1—C1—H1A | 110.0 | H12B—C12—H12C | 109.5 |
| C4—C1—H1A | 110.0 | Si3—C13—H13A | 109.5 |
| N1—C1—H1B | 110.0 | Si3—C13—H13B | 109.5 |
| C4—C1—H1B | 110.0 | H13A—C13—H13B | 109.5 |
| H1A—C1—H1B | 108.3 | Si3—C13—H13C | 109.5 |
| N2—C2—C5 | 108.29 (14) | H13A—C13—H13C | 109.5 |
| N2—C2—H2A | 110.0 | H13B—C13—H13C | 109.5 |
| C5—C2—H2A | 110.0 | Si3—C14—H14A | 109.5 |
| N2—C2—H2B | 110.0 | Si3—C14—H14B | 109.5 |
| C5—C2—H2B | 110.0 | H14A—C14—H14B | 109.5 |
| H2A—C2—H2B | 108.4 | Si3—C14—H14C | 109.5 |
| N3—C3—C6 | 108.65 (13) | H14A—C14—H14C | 109.5 |
| N3—C3—H3A | 110.0 | H14B—C14—H14C | 109.5 |
| C6—C3—H3A | 110.0 | Si3—C15—H15A | 109.5 |
| N3—C3—H3B | 110.0 | Si3—C15—H15B | 109.5 |
| C6—C3—H3B | 110.0 | H15A—C15—H15B | 109.5 |
| H3A—C3—H3B | 108.3 | Si3—C15—H15C | 109.5 |
| N4—C4—C1 | 108.64 (13) | H15A—C15—H15C | 109.5 |
| N4—C4—H4A | 110.0 | H15B—C15—H15C | 109.5 |
| C1—C4—H4A | 110.0 | Zr—C16—H16A | 109.5 |
| N4—C4—H4B | 110.0 | Zr—C16—H16B | 109.5 |
| C1—C4—H4B | 110.0 | H16A—C16—H16B | 109.5 |
| H4A—C4—H4B | 108.3 | Zr—C16—H16C | 109.5 |
| N4—C5—C2 | 107.87 (13) | H16A—C16—H16C | 109.5 |
| N4—C5—H5A | 110.1 | H16B—C16—H16C | 109.5 |
| C2—C5—H5A | 110.1 | | |
| | | | |
| N2—Zr—N1—C1 | −32.96 (13) | C1—N1—Si1—C8 | −37.01 (16) |
| N3—Zr—N1—C1 | 94.52 (12) | Zr—N1—Si1—C8 | 132.28 (12) |
| C16—Zr—N1—C1 | −150.64 (12) | C1—N1—Si1—C9 | −155.67 (13) |
| N4—Zr—N1—C1 | 29.95 (11) | Zr—N1—Si1—C9 | 13.62 (12) |

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| N2—Zr—N1—Si1 | 157.39 (8) | C2—N2—Si2—C12 | 74.34 (14) |
| N3—Zr—N1—Si1 | −75.14 (10) | Zr—N2—Si2—C12 | −106.18 (11) |
| C16—Zr—N1—Si1 | 39.70 (10) | C2—N2—Si2—C11 | −163.93 (12) |
| N4—Zr—N1—Si1 | −139.70 (10) | Zr—N2—Si2—C11 | 15.55 (12) |
| N1—Zr—N2—C2 | 92.84 (12) | C2—N2—Si2—C10 | −45.59 (15) |
| N3—Zr—N2—C2 | −34.49 (13) | Zr—N2—Si2—C10 | 133.89 (11) |
| C16—Zr—N2—C2 | −149.97 (12) | C3—N3—Si3—C13 | −26.69 (15) |
| N4—Zr—N2—C2 | 29.87 (11) | Zr—N3—Si3—C13 | 148.55 (10) |
| N1—Zr—N2—Si2 | −86.65 (10) | C3—N3—Si3—C14 | −145.46 (13) |
| N3—Zr—N2—Si2 | 146.03 (9) | Zr—N3—Si3—C14 | 29.77 (12) |
| C16—Zr—N2—Si2 | 30.54 (12) | C3—N3—Si3—C15 | 94.13 (14) |
| N4—Zr—N2—Si2 | −149.62 (11) | Zr—N3—Si3—C15 | −90.64 (11) |
| N2—Zr—N3—C3 | 92.41 (11) | Si1—N1—C1—C4 | 112.38 (14) |
| N1—Zr—N3—C3 | −35.93 (12) | Zr—N1—C1—C4 | −58.05 (17) |
| C16—Zr—N3—C3 | −151.18 (11) | Si2—N2—C2—C5 | 120.48 (13) |
| N4—Zr—N3—C3 | 28.37 (10) | Zr—N2—C2—C5 | −59.08 (16) |
| N2—Zr—N3—Si3 | −83.04 (9) | Si3—N3—C3—C6 | 119.29 (13) |
| N1—Zr—N3—Si3 | 148.62 (8) | Zr—N3—C3—C6 | −56.37 (16) |
| C16—Zr—N3—Si3 | 33.37 (10) | C6—N4—C4—C1 | −144.45 (14) |
| N4—Zr—N3—Si3 | −147.08 (9) | C5—N4—C4—C1 | 88.09 (15) |
| N2—Zr—N4—C4 | 121.87 (11) | Zr—N4—C4—C1 | −28.38 (15) |
| N1—Zr—N4—C4 | 0.34 (10) | N1—C1—C4—N4 | 54.78 (18) |
| N3—Zr—N4—C4 | −118.70 (11) | C4—N4—C5—C2 | −146.42 (14) |
| N2—Zr—N4—C6 | −117.57 (11) | C6—N4—C5—C2 | 85.33 (15) |
| N1—Zr—N4—C6 | 120.91 (11) | Zr—N4—C5—C2 | −29.91 (15) |
| N3—Zr—N4—C6 | 1.87 (10) | N2—C2—C5—N4 | 56.44 (17) |
| N2—Zr—N4—C5 | 1.21 (10) | C4—N4—C6—C3 | 86.62 (16) |
| N1—Zr—N4—C5 | −120.31 (11) | C5—N4—C6—C3 | −145.17 (14) |
| N3—Zr—N4—C5 | 120.65 (11) | Zr—N4—C6—C3 | −29.71 (15) |
| C1—N1—Si1—C7 | 84.74 (16) | N3—C3—C6—N4 | 54.96 (18) |
| Zr—N1—Si1—C7 | −105.97 (12) | | |