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Crystal structure of a zwitterionic azaallyl zirconiumamide complex bearing a Zr^{+}-μ-CH_3—B^{-} moiety and one equivalent of *n*-hexane as a solvent

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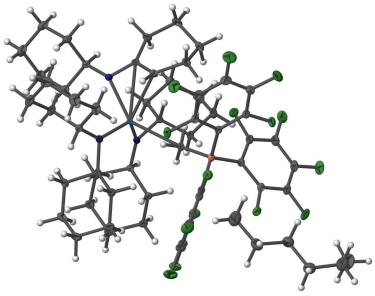
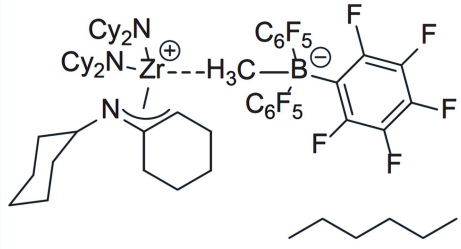
Structural data: full structural data are available from iucrdata.iucr.org

The zirconiumamide complex [(cyclohex-1-enyl)cyclohexylamido]bis(dicyclohexylamido)[methyltris(pentafluorophenyl)borato]zirconium(IV) hexane monosolvate, $[Zr\{N(C_6H_{11})_2\}_2\{N(C_6H_{11})(C_6H_9)\}\{BCH_3(C_6F_5)_3\}]\cdot C_6H_{14}$, is zwitterionic and bears a Zr^{+}—μ-CH_3—B^{-} moiety. The reaction of tris(dicyclohexylamido)methylzirconium with the strong Lewis acid tris(pentafluorophenyl)borane results in the formation of an azaallyl zirconium motif by the loss of H_2 in one dicyclohexylamido ligand, as shown by single-crystal X-ray diffraction. The Zr^{IV} cation is coordinated to the N atoms of two dicyclohexylamido ligands, the π-system of one azaallyl ligand, and to the μ-CH_3—B unit, resulting in a distorted tetrahedral coordination environment. The Zr—N distance to the azaallyl ligand is elongated, whereas the Zr—C distance to this moiety is found to be shortened in comparison with those to the two Cy_2N groups (Cy is C_6H_{11}).

3D view



Chemical scheme



Structure description

Highly electrophilic d^0 cations of group 4 metals are of great academic and industrial interest (Bochmann, 2010), because they are considered to be one of the active species in polyolefin chemistry (Jordan, 1991). In Ziegler-type polymerization processes, boranes and aluminium derivatives, *e.g.* methylalumoxan (MAO), are used to activate the precatalysts (Bochmann, 1996, 2004). Such strong Lewis acids are well known to abstract alkyl moieties to generate highly electrophilic Cp_2MR (M = Ti, Zr; R = CH_3) cations (Bochmann, 2010; Erker, 2005; Pellecchia *et al.*, 1995). Recently, we reported the formation of non-metallocene cations by abstraction of methyl groups from tris(dicyclohexylamido)methyl complexes of group 4 metals using tris(pentafluorophenyl)-borane (Adler *et al.*, 2016). In this context, the formation of d^0 metal olefin complexes is

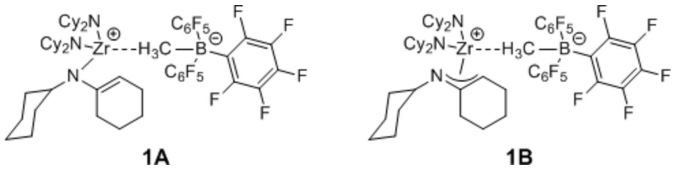


Figure 1
κ^1-Enamido (**1A**) *versus* η^3-azaallyl (**1B**) bonding modes found in azaallyl complexes.

of general interest, but azaallyl metal complexes seem to be an acceptable compromise, particularly due to their different bonding modes, from κ^1-enamido (**1 A**) up to η^3-azaallyl moieties (**1B**) (Yuan *et al.*, 2010; Fig. 1).

Compound **1** crystallizes with one *n*-hexane solvent molecule. Fig. 2 shows the molecular structure of **1**. The C37 methyl group is abstracted by the tris(pentafluorophenyl)borane moiety. The Zr1···C37 bond length of 2.6616 (10) Å is considerably elongated in comparison with a Zr—C single bond of 2.286 (3) Å (Adler *et al.*, 2014), and a new C37—B1 single bond of 1.6788 (14) Å is formed (Pyykkö & Atsumi, 2009). In contrast to our recently published results (Adler *et al.*, 2016), the formation of a C═C bond under abstraction of H_2 in one ligand was observed, giving rise to an azaallyl zirconium complex. The corresponding C31—C36 bond is significantly shortened to 1.3991 (14) Å compared to 1.5273 (85) Å (Adler *et al.*, 2016). The bond lengths Zr1—C36 of 2.5013 (10) Å and Zr1—N3 of 2.1524 (8) Å are similar to those found in other azaallyl zirconium complexes (Yuan *et al.*, 2017). Additionally, the Zr1—N3—C31 bond angle is significantly narrowed to 91.97 (6)° compared to 103.8 (3)° (Adler *et al.*, 2016), which underlines the coordination mode as an azaallyl ligand. The bond lengths to the N atoms of the dicyclohexylamido ligands [Zr1—N1 = 2.0321 (8), Zr1—N2 = 2.0242 (8) Å] lie within the range of comparable compounds (Adler *et al.*, 2016) but are slightly shortened in comparison to the starting material [Zr1—N1 = 2.048 (2), Zr1—N2 = 2.054 (2) Å; Adler *et al.*, 2014]. This indicates increased Lewis acidity of the zirconium cation resulting in stronger Zr(d_π)—N(p_π) interactions. The nitrogen atoms N1 and N2 are coordinated trigonally planar as shown by the sum of angles (N1: 359.34°, N2: 359.99°). Nitrogen atom N3 is coordinated in a slightly distorted trigonal–planar fashion (sum of angles: 349.17°), which can be explained by its participation within the azaallylic coordination mode of the ligand.

No significant supramolecular features are observed. The crystal packing (Fig. 3) appears to be dominated by van der Waals interactions alone.

Synthesis and crystallization

All reactions were carried out under a dry nitrogen atmosphere using Schlenk techniques or in a glove box. The starting zirconium complex and the tris(pentafluorphenyl)-borane were prepared according to published procedures (Adler *et al.*, 2014; Behrends *et al.*, 2016). Solvents were dried according to standard procedures over Na/K alloy with benzophenone as indicator and distilled under a nitrogen atmosphere.

Tris(dicyclohexylamido)methylzirconium and tris(pentafluorophenyl)borane were dissolved in *n*-hexane. After a few minutes a yellow solid began to precipitate. The solvent was decanted and stored in a separate flask at 243 K. Crystals suitable for X-ray diffraction were obtained from this mother liquor.

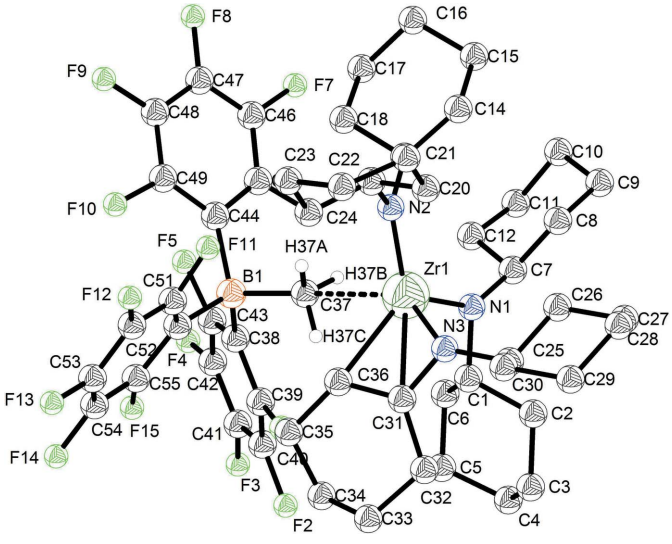


Figure 2
Solid-state molecular structure of complex **1**. Displacement ellipsoids correspond to the 50% probability level. H atoms except for those of the CH_3 group have been omitted for clarity.

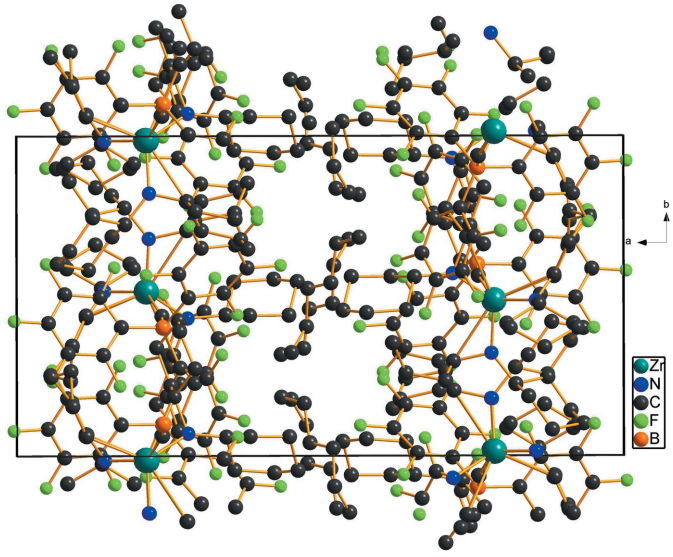


Figure 3
A view along the *c* axis showing the packing of molecules in the crystal structure of compound 1 and *n*-hexane. No significant supramolecular features can be observed. Color code: C grey, H white, B orange, F bright-green, N blue, Zr dark-green spheres.

Table 1
Experimental details.

Crystal data	
Chemical formula	$[Zr(C_{19}F_{18}B)(C_{12}H_{22}N)_2$-$(C_{12}H_{20}N)]\cdot C_6H_{14}$
M_r	1243.31
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	23.4930 (15), 11.9942 (8), 21.8489 (14)
β (°)	104.2591 (19)
V (Å^3)	5966.9 (7)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.27
Crystal size (mm)	0.25 × 0.20 × 0.10
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.977, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	345389, 26205, 21238
R_{int}	0.054
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.806
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.031, 0.084, 1.04
No. of reflections	26205
No. of parameters	748
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.29, −0.52

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXS2013* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 2006) and *publCIF* (Westrip, 2010).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

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full crystallographic data

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[(Cyclohex-1-enyl)cyclohexylamido]bis(dicyclohexylamido)[methyltris(pentafluorophenyl)borato]zirconium(IV) hexane monosolvate

Crystal data

$[Zr(C_{19}F_{18}B)(C_{12}H_{22}N)_2(C_{12}H_{20}N)]\cdot C_6H_{14}$
M_r = 1243.31
Monoclinic, $P2_1/c$
a = 23.4930 (15) Å
b = 11.9942 (8) Å
c = 21.8489 (14) Å
β = 104.2591 (19)°
V = 5966.9 (7) Å^3
Z = 4
$F(000)$ = 2592
D_x = 1.384 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9306 reflections
θ = 2.2–33.6°
μ = 0.27 mm^{-1}
T = 100 K
Block, colourless
0.25 × 0.20 × 0.10 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: sealed tube
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min} = 0.977, T_{max} = 1.000
345389 measured reflections
26205 independent reflections
21238 reflections with $I > 2\sigma(I)$
R_{int} = 0.054
θ_{max} = 35.0°, θ_{min} = 1.8°
h = −37→36
k = −19→19
l = −35→35

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.084
S = 1.04
26205 reflections
748 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.040P)^2 + 2.P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 1.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.52 e Å^{-3}

Special details

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

Refinement. The hydrogen atoms of the bridging methyl group (C37) were clearly discernible from a difference map and were refined freely.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Zr1	0.21383 (2)	0.48636 (2)	0.38286 (2)	0.00850 (2)
N1	0.28171 (3)	0.57005 (6)	0.36166 (4)	0.01011 (12)
N2	0.21802 (3)	0.32108 (6)	0.40219 (4)	0.01157 (13)
N3	0.14480 (3)	0.48570 (7)	0.29728 (4)	0.01232 (13)
C1	0.25874 (4)	0.68504 (7)	0.34853 (4)	0.01084 (14)
H1	0.2180	0.6846	0.3547	0.013*
C2	0.25333 (4)	0.71999 (8)	0.27962 (4)	0.01353 (16)
H2A	0.2924	0.7142	0.2703	0.016*
H2B	0.2265	0.6677	0.2513	0.016*
C3	0.23021 (5)	0.83900 (8)	0.26558 (5)	0.01677 (17)
H3A	0.2313	0.8592	0.2220	0.020*
H3B	0.1888	0.8422	0.2683	0.020*
C4	0.26633 (5)	0.92320 (8)	0.31160 (5)	0.01873 (19)
H4A	0.2488	0.9983	0.3027	0.022*
H4B	0.3068	0.9260	0.3059	0.022*
C5	0.26799 (5)	0.89024 (8)	0.37963 (5)	0.01808 (18)
H5A	0.2277	0.8928	0.3860	0.022*
H5B	0.2924	0.9443	0.4090	0.022*
C6	0.29323 (4)	0.77286 (7)	0.39441 (4)	0.01356 (16)
H6A	0.2923	0.7527	0.4381	0.016*
H6B	0.3347	0.7725	0.3919	0.016*
C7	0.34477 (4)	0.55940 (7)	0.36306 (4)	0.01105 (14)
H7	0.3556	0.6262	0.3410	0.013*
C8	0.35808 (4)	0.45651 (8)	0.32758 (4)	0.01307 (15)
H8A	0.3354	0.4606	0.2830	0.016*
H8B	0.3455	0.3888	0.3465	0.016*
C9	0.42381 (4)	0.44768 (9)	0.33006 (5)	0.01716 (17)
H9A	0.4313	0.3758	0.3112	0.021*
H9B	0.4347	0.5084	0.3044	0.021*
C10	0.46252 (4)	0.45513 (9)	0.39729 (5)	0.01722 (17)
H10A	0.4559	0.3888	0.4216	0.021*
H10B	0.5044	0.4559	0.3960	0.021*
C11	0.44859 (4)	0.56039 (8)	0.42992 (5)	0.01702 (18)
H11A	0.4575	0.6270	0.4072	0.020*
H11B	0.4733	0.5631	0.4737	0.020*
C12	0.38364 (4)	0.56092 (8)	0.43076 (4)	0.01395 (16)
H12A	0.3749	0.6284	0.4529	0.017*

H12B	0.3749	0.4948	0.4540	0.017*
C13	0.28052 (4)	0.29532 (7)	0.43064 (4)	0.01154 (15)
H13	0.3031	0.3648	0.4275	0.014*
C14	0.30406 (4)	0.20484 (8)	0.39345 (5)	0.01518 (16)
H14A	0.2804	0.1363	0.3925	0.018*
H14B	0.2990	0.2304	0.3493	0.018*
C15	0.36868 (5)	0.17665 (9)	0.42115 (6)	0.0209 (2)
H15A	0.3799	0.1129	0.3978	0.025*
H15B	0.3932	0.2413	0.4159	0.025*
C16	0.38043 (5)	0.14722 (9)	0.49106 (6)	0.0231 (2)
H16A	0.4230	0.1350	0.5084	0.028*
H16B	0.3597	0.0773	0.4961	0.028*
C17	0.35950 (5)	0.24079 (9)	0.52747 (5)	0.01961 (19)
H17A	0.3824	0.3092	0.5249	0.024*
H17B	0.3667	0.2195	0.5725	0.024*
C18	0.29389 (4)	0.26501 (8)	0.50108 (4)	0.01461 (16)
H18A	0.2820	0.3274	0.5249	0.018*
H18B	0.2707	0.1985	0.5067	0.018*
C19	0.17799 (4)	0.22409 (7)	0.39555 (4)	0.01309 (15)
H19	0.2007	0.1611	0.4200	0.016*
C20	0.15693 (5)	0.18612 (9)	0.32690 (5)	0.01965 (19)
H20A	0.1913	0.1695	0.3099	0.024*
H20B	0.1344	0.2471	0.3014	0.024*
C21	0.11804 (6)	0.08198 (10)	0.32142 (6)	0.0261 (2)
H21A	0.1030	0.0623	0.2763	0.031*
H21B	0.1419	0.0186	0.3428	0.031*
C22	0.06636 (5)	0.10117 (10)	0.35104 (7)	0.0282 (3)
H22A	0.0396	0.1574	0.3260	0.034*
H22B	0.0441	0.0308	0.3500	0.034*
C23	0.08721 (5)	0.14104 (10)	0.41874 (7)	0.0275 (2)
H23A	0.1103	0.0813	0.4448	0.033*
H23B	0.0528	0.1574	0.4358	0.033*
C24	0.12520 (5)	0.24595 (10)	0.42288 (6)	0.0240 (2)
H24A	0.1014	0.3074	0.3993	0.029*
H24B	0.1390	0.2692	0.4676	0.029*
C25	0.14010 (4)	0.47556 (8)	0.22905 (4)	0.01350 (15)
H25	0.1389	0.5520	0.2105	0.016*
C26	0.19286 (4)	0.41361 (9)	0.21705 (5)	0.01617 (17)
H26A	0.1958	0.3393	0.2373	0.019*
H26B	0.2292	0.4555	0.2362	0.019*
C27	0.18728 (5)	0.39968 (10)	0.14616 (5)	0.0226 (2)
H27A	0.1880	0.4740	0.1266	0.027*
H27B	0.2212	0.3565	0.1396	0.027*
C28	0.13047 (6)	0.33967 (11)	0.11418 (6)	0.0280 (2)
H28A	0.1270	0.3356	0.0681	0.034*
H28B	0.1316	0.2626	0.1306	0.034*
C29	0.07725 (5)	0.40048 (11)	0.12628 (5)	0.0264 (2)
H29A	0.0412	0.3578	0.1073	0.032*

H29B	0.0738	0.4748	0.1060	0.032*
C30	0.08306 (4)	0.41416 (9)	0.19716 (5)	0.01860 (18)
H30A	0.0828	0.3398	0.2167	0.022*
H30B	0.0490	0.4567	0.2039	0.022*
C31	0.11490 (4)	0.56706 (8)	0.31930 (4)	0.01275 (15)
C32	0.09037 (4)	0.66758 (8)	0.27946 (5)	0.01662 (17)
H32A	0.0640	0.6416	0.2394	0.020*
H32B	0.1232	0.7088	0.2689	0.020*
C33	0.05627 (5)	0.74724 (10)	0.31204 (6)	0.0228 (2)
H33A	0.0510	0.8197	0.2897	0.027*
H33B	0.0169	0.7159	0.3100	0.027*
C34	0.08872 (5)	0.76523 (9)	0.38072 (5)	0.02014 (19)
H34A	0.0680	0.8220	0.4001	0.024*
H34B	0.1289	0.7927	0.3831	0.024*
C35	0.09169 (4)	0.65535 (8)	0.41668 (5)	0.01687 (17)
H35A	0.1177	0.6645	0.4595	0.020*
H35B	0.0520	0.6360	0.4213	0.020*
C36	0.11457 (4)	0.56144 (8)	0.38317 (5)	0.01355 (16)
H36	0.1127 (7)	0.4872 (12)	0.4000 (7)	0.021 (4)*
F1	0.20245 (3)	0.79665 (5)	0.49768 (3)	0.01950 (12)
F2	0.24113 (4)	1.00298 (5)	0.51775 (4)	0.02520 (14)
F3	0.32734 (3)	1.05569 (6)	0.62319 (4)	0.02749 (15)
F4	0.37413 (3)	0.89050 (6)	0.70609 (3)	0.02459 (14)
F5	0.33760 (3)	0.68372 (5)	0.68722 (3)	0.01849 (12)
F6	0.36335 (3)	0.55919 (5)	0.57935 (3)	0.01821 (12)
F7	0.43464 (3)	0.40442 (6)	0.64374 (3)	0.02380 (14)
F8	0.39619 (3)	0.26123 (6)	0.72163 (4)	0.02996 (16)
F9	0.28489 (3)	0.28137 (6)	0.73580 (3)	0.02515 (14)
F10	0.21304 (3)	0.43460 (5)	0.67477 (3)	0.01726 (11)
F11	0.16097 (3)	0.41066 (5)	0.54666 (3)	0.01937 (12)
F12	0.04898 (3)	0.39981 (6)	0.54976 (4)	0.02976 (16)
F13	−0.00419 (3)	0.57798 (8)	0.59065 (5)	0.03586 (19)
F14	0.05897 (3)	0.76766 (7)	0.62731 (4)	0.02899 (16)
F15	0.16986 (3)	0.78129 (5)	0.62573 (3)	0.01876 (12)
C37	0.23938 (4)	0.56284 (8)	0.50084 (4)	0.01287 (15)
H37A	0.2235 (7)	0.4879 (13)	0.4941 (8)	0.025 (4)*
H37B	0.2776 (7)	0.5660 (13)	0.4939 (7)	0.022 (4)*
H37C	0.2143 (7)	0.6116 (13)	0.4725 (8)	0.026 (4)*
C38	0.26937 (4)	0.72498 (8)	0.58933 (4)	0.01252 (15)
C39	0.24776 (4)	0.81354 (8)	0.54883 (5)	0.01474 (16)
C40	0.26623 (5)	0.92305 (8)	0.55851 (5)	0.01733 (18)
C41	0.30925 (5)	0.95006 (8)	0.61195 (5)	0.01906 (19)
C42	0.33261 (5)	0.86644 (9)	0.65361 (5)	0.01749 (18)
C43	0.31263 (4)	0.75757 (8)	0.64181 (5)	0.01405 (16)
C44	0.28281 (4)	0.50457 (7)	0.62061 (4)	0.01195 (15)
C45	0.34091 (4)	0.49069 (8)	0.61689 (4)	0.01361 (15)
C46	0.37951 (4)	0.41240 (8)	0.65014 (5)	0.01644 (17)
C47	0.36038 (5)	0.34000 (9)	0.69010 (5)	0.01923 (19)

C48	0.30397 (5)	0.35025 (8)	0.69660 (5)	0.01701 (18)
C49	0.26689 (4)	0.43110 (8)	0.66291 (4)	0.01347 (15)
C50	0.17245 (4)	0.59754 (8)	0.58320 (4)	0.01208 (15)
C51	0.13726 (4)	0.50347 (8)	0.56545 (5)	0.01491 (16)
C52	0.07909 (5)	0.49462 (9)	0.56712 (5)	0.02023 (19)
C53	0.05214 (5)	0.58430 (10)	0.58782 (6)	0.0226 (2)
C54	0.08425 (5)	0.67975 (9)	0.60659 (5)	0.01938 (19)
C55	0.14281 (4)	0.68436 (8)	0.60441 (5)	0.01447 (16)
B1	0.24097 (5)	0.59861 (8)	0.57553 (5)	0.01129 (16)
C56	0.43620 (8)	0.81659 (16)	0.54449 (9)	0.0517 (5)
H56A	0.4564	0.8474	0.5141	0.078*
H56B	0.3981	0.8535	0.5393	0.078*
H56C	0.4302	0.7364	0.5371	0.078*
C57	0.47325 (6)	0.83595 (12)	0.61115 (8)	0.0339 (3)
H57A	0.5119	0.7997	0.6157	0.041*
H57B	0.4538	0.8001	0.6414	0.041*
C58	0.48270 (6)	0.95890 (11)	0.62787 (6)	0.0285 (2)
H58A	0.4441	0.9950	0.6243	0.034*
H58B	0.5016	0.9953	0.5973	0.034*
C59	0.52089 (6)	0.97624 (12)	0.69449 (7)	0.0322 (3)
H59A	0.5060	0.9280	0.7238	0.039*
H59B	0.5614	0.9518	0.6956	0.039*
C60	0.52295 (7)	1.09536 (13)	0.71790 (7)	0.0362 (3)
H60A	0.4826	1.1190	0.7180	0.043*
H60B	0.5469	1.0978	0.7621	0.043*
C61	0.54768 (9)	1.17644 (15)	0.67981 (9)	0.0493 (4)
H61A	0.5866	1.1512	0.6769	0.074*
H61B	0.5511	1.2498	0.7001	0.074*
H61C	0.5216	1.1817	0.6373	0.074*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zr1	0.00881 (4)	0.00682 (3)	0.00962 (4)	0.00034 (3)	0.00177 (3)	0.00068 (3)
N1	0.0106 (3)	0.0086 (3)	0.0109 (3)	0.0005 (2)	0.0023 (2)	0.0006 (2)
N2	0.0121 (3)	0.0083 (3)	0.0135 (3)	−0.0007 (2)	0.0016 (3)	0.0007 (2)
N3	0.0110 (3)	0.0123 (3)	0.0126 (3)	0.0012 (2)	0.0007 (3)	−0.0004 (3)
C1	0.0119 (4)	0.0084 (3)	0.0121 (3)	0.0002 (3)	0.0028 (3)	0.0009 (3)
C2	0.0178 (4)	0.0107 (3)	0.0113 (4)	0.0002 (3)	0.0022 (3)	0.0018 (3)
C3	0.0215 (5)	0.0119 (4)	0.0156 (4)	0.0010 (3)	0.0020 (3)	0.0038 (3)
C4	0.0273 (5)	0.0100 (4)	0.0181 (4)	−0.0009 (3)	0.0042 (4)	0.0027 (3)
C5	0.0275 (5)	0.0097 (4)	0.0169 (4)	0.0009 (3)	0.0053 (4)	−0.0007 (3)
C6	0.0182 (4)	0.0094 (3)	0.0126 (4)	−0.0009 (3)	0.0031 (3)	−0.0005 (3)
C7	0.0101 (3)	0.0113 (3)	0.0114 (3)	−0.0001 (3)	0.0019 (3)	0.0010 (3)
C8	0.0127 (4)	0.0133 (4)	0.0133 (4)	0.0004 (3)	0.0035 (3)	−0.0010 (3)
C9	0.0141 (4)	0.0206 (4)	0.0176 (4)	0.0029 (3)	0.0054 (3)	−0.0002 (3)
C10	0.0122 (4)	0.0169 (4)	0.0214 (4)	0.0021 (3)	0.0017 (3)	0.0012 (3)
C11	0.0133 (4)	0.0150 (4)	0.0198 (4)	−0.0006 (3)	−0.0015 (3)	0.0003 (3)

C12	0.0138 (4)	0.0135 (4)	0.0129 (4)	0.0006 (3)	0.0000 (3)	−0.0005 (3)
C13	0.0129 (4)	0.0080 (3)	0.0132 (4)	−0.0003 (3)	0.0021 (3)	0.0010 (3)
C14	0.0170 (4)	0.0108 (4)	0.0182 (4)	0.0014 (3)	0.0052 (3)	−0.0002 (3)
C15	0.0173 (4)	0.0165 (4)	0.0299 (5)	0.0042 (3)	0.0078 (4)	0.0011 (4)
C16	0.0187 (5)	0.0176 (4)	0.0299 (6)	0.0057 (4)	−0.0001 (4)	0.0036 (4)
C17	0.0190 (5)	0.0157 (4)	0.0200 (4)	0.0004 (3)	−0.0030 (4)	0.0020 (3)
C18	0.0175 (4)	0.0116 (4)	0.0134 (4)	−0.0003 (3)	0.0013 (3)	0.0013 (3)
C19	0.0131 (4)	0.0091 (3)	0.0159 (4)	−0.0019 (3)	0.0013 (3)	−0.0001 (3)
C20	0.0240 (5)	0.0152 (4)	0.0177 (4)	−0.0050 (3)	0.0014 (4)	−0.0029 (3)
C21	0.0286 (6)	0.0180 (5)	0.0284 (6)	−0.0085 (4)	0.0004 (4)	−0.0071 (4)
C22	0.0168 (5)	0.0203 (5)	0.0420 (7)	−0.0060 (4)	−0.0029 (5)	−0.0006 (5)
C23	0.0217 (5)	0.0238 (5)	0.0394 (7)	−0.0101 (4)	0.0122 (5)	−0.0046 (5)
C24	0.0214 (5)	0.0196 (5)	0.0344 (6)	−0.0083 (4)	0.0134 (4)	−0.0088 (4)
C25	0.0128 (4)	0.0142 (4)	0.0121 (4)	0.0002 (3)	0.0004 (3)	−0.0002 (3)
C26	0.0149 (4)	0.0183 (4)	0.0148 (4)	0.0012 (3)	0.0026 (3)	−0.0018 (3)
C27	0.0254 (5)	0.0268 (5)	0.0164 (4)	0.0013 (4)	0.0071 (4)	−0.0027 (4)
C28	0.0320 (6)	0.0316 (6)	0.0182 (5)	−0.0011 (5)	0.0019 (4)	−0.0091 (4)
C29	0.0238 (5)	0.0326 (6)	0.0176 (5)	−0.0013 (4)	−0.0046 (4)	−0.0050 (4)
C30	0.0137 (4)	0.0214 (4)	0.0180 (4)	−0.0011 (3)	−0.0012 (3)	−0.0025 (3)
C31	0.0096 (4)	0.0122 (4)	0.0153 (4)	0.0003 (3)	0.0008 (3)	0.0003 (3)
C32	0.0156 (4)	0.0151 (4)	0.0178 (4)	0.0045 (3)	0.0013 (3)	0.0031 (3)
C33	0.0216 (5)	0.0203 (5)	0.0248 (5)	0.0113 (4)	0.0026 (4)	0.0023 (4)
C34	0.0215 (5)	0.0154 (4)	0.0238 (5)	0.0061 (3)	0.0059 (4)	−0.0011 (4)
C35	0.0149 (4)	0.0166 (4)	0.0204 (4)	0.0024 (3)	0.0067 (3)	−0.0010 (3)
C36	0.0119 (4)	0.0128 (4)	0.0162 (4)	0.0014 (3)	0.0039 (3)	0.0014 (3)
F1	0.0233 (3)	0.0142 (3)	0.0177 (3)	−0.0008 (2)	−0.0013 (2)	0.0011 (2)
F2	0.0368 (4)	0.0115 (3)	0.0270 (3)	−0.0009 (2)	0.0073 (3)	0.0044 (2)
F3	0.0334 (4)	0.0130 (3)	0.0371 (4)	−0.0104 (3)	0.0105 (3)	−0.0063 (3)
F4	0.0237 (3)	0.0242 (3)	0.0232 (3)	−0.0077 (3)	0.0007 (3)	−0.0101 (3)
F5	0.0210 (3)	0.0176 (3)	0.0147 (3)	0.0001 (2)	0.0001 (2)	−0.0012 (2)
F6	0.0159 (3)	0.0212 (3)	0.0193 (3)	−0.0010 (2)	0.0078 (2)	0.0058 (2)
F7	0.0141 (3)	0.0270 (3)	0.0295 (4)	0.0036 (2)	0.0039 (3)	0.0033 (3)
F8	0.0273 (4)	0.0245 (3)	0.0328 (4)	0.0063 (3)	−0.0025 (3)	0.0131 (3)
F9	0.0311 (4)	0.0238 (3)	0.0198 (3)	−0.0056 (3)	0.0047 (3)	0.0111 (3)
F10	0.0178 (3)	0.0202 (3)	0.0159 (3)	−0.0031 (2)	0.0081 (2)	0.0020 (2)
F11	0.0224 (3)	0.0139 (3)	0.0240 (3)	−0.0043 (2)	0.0099 (2)	−0.0063 (2)
F12	0.0204 (3)	0.0278 (4)	0.0413 (4)	−0.0127 (3)	0.0079 (3)	−0.0083 (3)
F13	0.0128 (3)	0.0442 (5)	0.0530 (5)	−0.0039 (3)	0.0128 (3)	−0.0078 (4)
F14	0.0198 (3)	0.0311 (4)	0.0379 (4)	0.0070 (3)	0.0107 (3)	−0.0101 (3)
F15	0.0190 (3)	0.0147 (3)	0.0234 (3)	−0.0008 (2)	0.0069 (2)	−0.0062 (2)
C37	0.0160 (4)	0.0114 (4)	0.0117 (4)	0.0004 (3)	0.0043 (3)	−0.0004 (3)
C38	0.0139 (4)	0.0117 (4)	0.0127 (4)	−0.0015 (3)	0.0045 (3)	−0.0009 (3)
C39	0.0178 (4)	0.0119 (4)	0.0146 (4)	−0.0016 (3)	0.0040 (3)	−0.0007 (3)
C40	0.0228 (5)	0.0110 (4)	0.0196 (4)	−0.0017 (3)	0.0078 (4)	0.0008 (3)
C41	0.0228 (5)	0.0122 (4)	0.0242 (5)	−0.0064 (3)	0.0097 (4)	−0.0047 (3)
C42	0.0176 (4)	0.0167 (4)	0.0186 (4)	−0.0049 (3)	0.0052 (3)	−0.0061 (3)
C43	0.0153 (4)	0.0136 (4)	0.0138 (4)	−0.0017 (3)	0.0047 (3)	−0.0020 (3)
C44	0.0138 (4)	0.0118 (4)	0.0105 (3)	−0.0013 (3)	0.0036 (3)	−0.0004 (3)

C45	0.0151 (4)	0.0131 (4)	0.0126 (4)	−0.0012 (3)	0.0035 (3)	0.0011 (3)
C46	0.0136 (4)	0.0173 (4)	0.0173 (4)	0.0009 (3)	0.0017 (3)	0.0003 (3)
C47	0.0207 (5)	0.0160 (4)	0.0180 (4)	0.0015 (3)	−0.0010 (4)	0.0042 (3)
C48	0.0227 (5)	0.0151 (4)	0.0121 (4)	−0.0035 (3)	0.0022 (3)	0.0039 (3)
C49	0.0162 (4)	0.0131 (4)	0.0115 (4)	−0.0028 (3)	0.0042 (3)	−0.0005 (3)
C50	0.0127 (4)	0.0128 (4)	0.0111 (3)	−0.0007 (3)	0.0035 (3)	−0.0006 (3)
C51	0.0155 (4)	0.0154 (4)	0.0144 (4)	−0.0018 (3)	0.0047 (3)	−0.0022 (3)
C52	0.0157 (4)	0.0224 (5)	0.0225 (5)	−0.0066 (3)	0.0044 (4)	−0.0032 (4)
C53	0.0113 (4)	0.0301 (5)	0.0270 (5)	−0.0018 (4)	0.0057 (4)	−0.0029 (4)
C54	0.0152 (4)	0.0232 (5)	0.0206 (5)	0.0032 (3)	0.0060 (4)	−0.0040 (4)
C55	0.0144 (4)	0.0152 (4)	0.0140 (4)	−0.0002 (3)	0.0038 (3)	−0.0023 (3)
B1	0.0129 (4)	0.0107 (4)	0.0109 (4)	−0.0012 (3)	0.0042 (3)	−0.0005 (3)
C56	0.0418 (9)	0.0492 (10)	0.0592 (11)	−0.0040 (7)	0.0033 (8)	−0.0231 (8)
C57	0.0257 (6)	0.0294 (6)	0.0467 (8)	0.0033 (5)	0.0093 (6)	−0.0049 (6)
C58	0.0251 (6)	0.0279 (6)	0.0310 (6)	0.0036 (4)	0.0038 (5)	−0.0008 (5)
C59	0.0312 (6)	0.0309 (6)	0.0318 (6)	0.0031 (5)	0.0022 (5)	0.0012 (5)
C60	0.0390 (8)	0.0346 (7)	0.0340 (7)	−0.0014 (6)	0.0072 (6)	−0.0023 (5)
C61	0.0575 (11)	0.0405 (9)	0.0476 (9)	−0.0147 (8)	0.0085 (8)	0.0021 (7)

Geometric parameters (Å, º)

Zr1—N2	2.0242 (8)	C27—H27A	0.9900
Zr1—N1	2.0321 (8)	C27—H27B	0.9900
Zr1—N3	2.1524 (8)	C28—C29	1.5258 (19)
Zr1—H37A	2.384 (16)	C28—H28A	0.9900
N1—C7	1.4797 (12)	C28—H28B	0.9900
N1—C1	1.4831 (11)	C29—C30	1.5296 (16)
N2—C13	1.4792 (12)	C29—H29A	0.9900
N2—C19	1.4805 (12)	C29—H29B	0.9900
N3—C31	1.3578 (12)	C30—H30A	0.9900
N3—C25	1.4724 (12)	C30—H30B	0.9900
C1—C2	1.5377 (13)	C31—C36	1.3991 (14)
C1—C6	1.5397 (13)	C31—C32	1.5153 (13)
C1—H1	1.0000	C32—C33	1.5304 (15)
C2—C3	1.5312 (13)	C32—H32A	0.9900
C2—H2A	0.9900	C32—H32B	0.9900
C2—H2B	0.9900	C33—C34	1.5220 (16)
C3—C4	1.5268 (14)	C33—H33A	0.9900
C3—H3A	0.9900	C33—H33B	0.9900
C3—H3B	0.9900	C34—C35	1.5271 (15)
C4—C5	1.5294 (15)	C34—H34A	0.9900
C4—H4A	0.9900	C34—H34B	0.9900
C4—H4B	0.9900	C35—C36	1.5124 (14)
C5—C6	1.5309 (13)	C35—H35A	0.9900
C5—H5A	0.9900	C35—H35B	0.9900
C5—H5B	0.9900	C36—H36	0.968 (15)
C6—H6A	0.9900	F1—C39	1.3554 (11)
C6—H6B	0.9900	F2—C40	1.3422 (12)

C7—C8	1.5300 (13)	F3—C41	1.3396 (12)
C7—C12	1.5352 (13)	F4—C42	1.3412 (12)
C7—H7	1.0000	F5—C43	1.3515 (11)
C8—C9	1.5354 (14)	F6—C45	1.3559 (11)
C8—H8A	0.9900	F7—C46	1.3399 (12)
C8—H8B	0.9900	F8—C47	1.3377 (12)
C9—C10	1.5280 (14)	F9—C48	1.3438 (12)
C9—H9A	0.9900	F10—C49	1.3531 (12)
C9—H9B	0.9900	F11—C51	1.3530 (11)
C10—C11	1.5246 (15)	F12—C52	1.3435 (12)
C10—H10A	0.9900	F13—C53	1.3420 (13)
C10—H10B	0.9900	F14—C54	1.3423 (12)
C11—C12	1.5306 (14)	F15—C55	1.3515 (11)
C11—H11A	0.9900	C37—B1	1.6788 (14)
C11—H11B	0.9900	C37—H37A	0.971 (16)
C12—H12A	0.9900	C37—H37B	0.948 (16)
C12—H12B	0.9900	C37—H37C	0.944 (16)
C13—C18	1.5366 (13)	C38—C43	1.3880 (13)
C13—C14	1.5380 (13)	C38—C39	1.3957 (13)
C13—H13	1.0000	C38—B1	1.6535 (13)
C14—C15	1.5273 (15)	C39—C40	1.3830 (13)
C14—H14A	0.9900	C40—C41	1.3813 (15)
C14—H14B	0.9900	C41—C42	1.3747 (16)
C15—C16	1.5253 (17)	C42—C43	1.3900 (14)
C15—H15A	0.9900	C44—C49	1.3931 (13)
C15—H15B	0.9900	C44—C45	1.3972 (13)
C16—C17	1.5254 (16)	C44—B1	1.6527 (14)
C16—H16A	0.9900	C45—C46	1.3811 (13)
C16—H16B	0.9900	C46—C47	1.3827 (15)
C17—C18	1.5347 (14)	C47—C48	1.3726 (16)
C17—H17A	0.9900	C48—C49	1.3875 (14)
C17—H17B	0.9900	C50—C55	1.3940 (13)
C18—H18A	0.9900	C50—C51	1.3960 (13)
C18—H18B	0.9900	C50—B1	1.6591 (14)
C19—C24	1.5258 (15)	C51—C52	1.3801 (15)
C19—C20	1.5285 (14)	C52—C53	1.3797 (16)
C19—H19	1.0000	C53—C54	1.3768 (16)
C20—C21	1.5346 (15)	C54—C55	1.3893 (14)
C20—H20A	0.9900	C56—C57	1.519 (2)
C20—H20B	0.9900	C56—H56A	0.9800
C21—C22	1.527 (2)	C56—H56B	0.9800
C21—H21A	0.9900	C56—H56C	0.9800
C21—H21B	0.9900	C57—C58	1.5223 (19)
C22—C23	1.5165 (19)	C57—H57A	0.9900
C22—H22A	0.9900	C57—H57B	0.9900
C22—H22B	0.9900	C58—C59	1.5244 (19)
C23—C24	1.5323 (16)	C58—H58A	0.9900
C23—H23A	0.9900	C58—H58B	0.9900

C23—H23B	0.9900	C59—C60	1.514 (2)
C24—H24A	0.9900	C59—H59A	0.9900
C24—H24B	0.9900	C59—H59B	0.9900
C25—C26	1.5224 (14)	C60—C61	1.488 (2)
C25—C30	1.5375 (14)	C60—H60A	0.9900
C25—H25	1.0000	C60—H60B	0.9900
C26—C27	1.5310 (15)	C61—H61A	0.9800
C26—H26A	0.9900	C61—H61B	0.9800
C26—H26B	0.9900	C61—H61C	0.9800
C27—C28	1.5258 (17)		

N2—Zr1—N1	122.06 (3)	C25—C26—C27	110.92 (8)
N2—Zr1—N3	99.51 (3)	C25—C26—H26A	109.5
N1—Zr1—N3	105.63 (3)	C27—C26—H26A	109.5
N2—Zr1—H37A	78.9 (4)	C25—C26—H26B	109.5
N1—Zr1—H37A	110.2 (4)	C27—C26—H26B	109.5
N3—Zr1—H37A	138.4 (4)	H26A—C26—H26B	108.0
C7—N1—C1	113.52 (7)	C28—C27—C26	111.23 (10)
C7—N1—Zr1	142.24 (6)	C28—C27—H27A	109.4
C1—N1—Zr1	103.58 (5)	C26—C27—H27A	109.4
C13—N2—C19	114.70 (7)	C28—C27—H27B	109.4
C13—N2—Zr1	106.53 (5)	C26—C27—H27B	109.4
C19—N2—Zr1	138.76 (6)	H27A—C27—H27B	108.0
C31—N3—C25	120.11 (8)	C29—C28—C27	110.91 (10)
C31—N3—Zr1	91.97 (6)	C29—C28—H28A	109.5
C25—N3—Zr1	137.09 (6)	C27—C28—H28A	109.5
N1—C1—C2	112.41 (7)	C29—C28—H28B	109.5
N1—C1—C6	113.72 (7)	C27—C28—H28B	109.5
C2—C1—C6	110.75 (7)	H28A—C28—H28B	108.0
N1—C1—Zr1	45.22 (4)	C28—C29—C30	110.74 (9)
C2—C1—Zr1	123.50 (6)	C28—C29—H29A	109.5
C6—C1—Zr1	125.73 (6)	C30—C29—H29A	109.5
N1—C1—H1	106.5	C28—C29—H29B	109.5
C2—C1—H1	106.5	C30—C29—H29B	109.5
C6—C1—H1	106.5	H29A—C29—H29B	108.1
Zr1—C1—H1	61.3	C29—C30—C25	111.14 (9)
C3—C2—C1	112.96 (8)	C29—C30—H30A	109.4
C3—C2—H2A	109.0	C25—C30—H30A	109.4
C1—C2—H2A	109.0	C29—C30—H30B	109.4
C3—C2—H2B	109.0	C25—C30—H30B	109.4
C1—C2—H2B	109.0	H30A—C30—H30B	108.0
H2A—C2—H2B	107.8	N3—C31—C36	116.69 (8)
C4—C3—C2	111.87 (8)	N3—C31—C32	121.67 (9)
C4—C3—H3A	109.2	C36—C31—C32	121.10 (8)
C2—C3—H3A	109.2	N3—C31—Zr1	56.35 (5)
C4—C3—H3B	109.2	C36—C31—Zr1	70.80 (5)
C2—C3—H3B	109.2	C32—C31—Zr1	140.46 (7)
H3A—C3—H3B	107.9	C31—C32—C33	113.47 (9)

C3—C4—C5	110.24 (8)	C31—C32—H32A	108.9
C3—C4—H4A	109.6	C33—C32—H32A	108.9
C5—C4—H4A	109.6	C31—C32—H32B	108.9
C3—C4—H4B	109.6	C33—C32—H32B	108.9
C5—C4—H4B	109.6	H32A—C32—H32B	107.7
H4A—C4—H4B	108.1	C34—C33—C32	110.76 (8)
C4—C5—C6	111.00 (8)	C34—C33—H33A	109.5
C4—C5—H5A	109.4	C32—C33—H33A	109.5
C6—C5—H5A	109.4	C34—C33—H33B	109.5
C4—C5—H5B	109.4	C32—C33—H33B	109.5
C6—C5—H5B	109.4	H33A—C33—H33B	108.1
H5A—C5—H5B	108.0	C33—C34—C35	109.46 (9)
C5—C6—C1	112.17 (8)	C33—C34—H34A	109.8
C5—C6—H6A	109.2	C35—C34—H34A	109.8
C1—C6—H6A	109.2	C33—C34—H34B	109.8
C5—C6—H6B	109.2	C35—C34—H34B	109.8
C1—C6—H6B	109.2	H34A—C34—H34B	108.2
H6A—C6—H6B	107.9	C36—C35—C34	111.74 (9)
N1—C7—C8	112.80 (7)	C36—C35—H35A	109.3
N1—C7—C12	111.95 (8)	C34—C35—H35A	109.3
C8—C7—C12	110.51 (7)	C36—C35—H35B	109.3
N1—C7—H7	107.1	C34—C35—H35B	109.3
C8—C7—H7	107.1	H35A—C35—H35B	107.9
C12—C7—H7	107.1	C31—C36—C35	122.47 (8)
C7—C8—C9	111.53 (8)	C31—C36—Zr1	77.32 (6)
C7—C8—H8A	109.3	C35—C36—Zr1	135.40 (7)
C9—C8—H8A	109.3	C31—C36—H36	115.8 (9)
C7—C8—H8B	109.3	C35—C36—H36	116.4 (9)
C9—C8—H8B	109.3	Zr1—C36—H36	78.5 (9)
H8A—C8—H8B	108.0	B1—C37—Zr1	167.21 (7)
C10—C9—C8	112.65 (8)	B1—C37—H37A	107.5 (10)
C10—C9—H9A	109.1	Zr1—C37—H37A	63.0 (9)
C8—C9—H9A	109.1	B1—C37—H37B	110.5 (9)
C10—C9—H9B	109.1	Zr1—C37—H37B	81.7 (9)
C8—C9—H9B	109.1	H37A—C37—H37B	110.8 (13)
H9A—C9—H9B	107.8	B1—C37—H37C	109.9 (10)
C11—C10—C9	110.64 (8)	Zr1—C37—H37C	67.8 (10)
C11—C10—H10A	109.5	H37A—C37—H37C	108.6 (13)
C9—C10—H10A	109.5	H37B—C37—H37C	109.4 (13)
C11—C10—H10B	109.5	C43—C38—C39	112.78 (8)
C9—C10—H10B	109.5	C43—C38—B1	126.10 (8)
H10A—C10—H10B	108.1	C39—C38—B1	120.98 (8)
C10—C11—C12	109.78 (8)	F1—C39—C40	114.91 (9)
C10—C11—H11A	109.7	F1—C39—C38	119.87 (8)
C12—C11—H11A	109.7	C40—C39—C38	125.06 (9)
C10—C11—H11B	109.7	F2—C40—C41	120.24 (9)
C12—C11—H11B	109.7	F2—C40—C39	120.45 (9)
H11A—C11—H11B	108.2	C41—C40—C39	119.26 (9)

C11—C12—C7	110.28 (8)	F3—C41—C42	120.78 (10)
C11—C12—H12A	109.6	F3—C41—C40	120.65 (10)
C7—C12—H12A	109.6	C42—C41—C40	118.57 (9)
C11—C12—H12B	109.6	F4—C42—C41	119.79 (9)
C7—C12—H12B	109.6	F4—C42—C43	120.14 (10)
H12A—C12—H12B	108.1	C41—C42—C43	120.07 (9)
N2—C13—C18	114.02 (8)	F5—C43—C38	121.26 (8)
N2—C13—C14	111.98 (7)	F5—C43—C42	114.44 (8)
C18—C13—C14	110.55 (7)	C38—C43—C42	124.27 (9)
N2—C13—Zr1	43.36 (4)	C49—C44—C45	112.89 (8)
C18—C13—Zr1	121.31 (6)	C49—C44—B1	127.56 (8)
C14—C13—Zr1	127.99 (6)	C45—C44—B1	119.52 (8)
N2—C13—H13	106.6	F6—C45—C46	115.31 (9)
C18—C13—H13	106.6	F6—C45—C44	119.60 (8)
C14—C13—H13	106.6	C46—C45—C44	125.08 (9)
Zr1—C13—H13	63.5	F7—C46—C45	121.33 (9)
C15—C14—C13	113.48 (8)	F7—C46—C47	119.60 (9)
C15—C14—H14A	108.9	C45—C46—C47	119.06 (10)
C13—C14—H14A	108.9	F8—C47—C48	120.72 (10)
C15—C14—H14B	108.9	F8—C47—C46	120.50 (10)
C13—C14—H14B	108.9	C48—C47—C46	118.78 (9)
H14A—C14—H14B	107.7	F9—C48—C47	119.53 (9)
C16—C15—C14	111.42 (9)	F9—C48—C49	120.23 (10)
C16—C15—H15A	109.3	C47—C48—C49	120.24 (9)
C14—C15—H15A	109.3	F10—C49—C48	114.48 (8)
C16—C15—H15B	109.3	F10—C49—C44	121.59 (8)
C14—C15—H15B	109.3	C48—C49—C44	123.92 (9)
H15A—C15—H15B	108.0	C55—C50—C51	112.70 (9)
C15—C16—C17	110.48 (9)	C55—C50—B1	127.19 (8)
C15—C16—H16A	109.6	C51—C50—B1	120.07 (8)
C17—C16—H16A	109.6	F11—C51—C52	115.40 (9)
C15—C16—H16B	109.6	F11—C51—C50	119.30 (9)
C17—C16—H16B	109.6	C52—C51—C50	125.26 (9)
H16A—C16—H16B	108.1	F12—C52—C53	120.01 (10)
C16—C17—C18	111.49 (8)	F12—C52—C51	120.90 (10)
C16—C17—H17A	109.3	C53—C52—C51	119.08 (10)
C18—C17—H17A	109.3	F13—C53—C54	120.49 (11)
C16—C17—H17B	109.3	F13—C53—C52	120.56 (10)
C18—C17—H17B	109.3	C54—C53—C52	118.94 (10)
H17A—C17—H17B	108.0	F14—C54—C53	119.88 (10)
C17—C18—C13	111.08 (9)	F14—C54—C55	120.29 (10)
C17—C18—H18A	109.4	C53—C54—C55	119.83 (10)
C13—C18—H18A	109.4	F15—C55—C54	114.08 (9)
C17—C18—H18B	109.4	F15—C55—C50	121.74 (9)
C13—C18—H18B	109.4	C54—C55—C50	124.17 (9)
H18A—C18—H18B	108.0	C44—B1—C38	111.28 (7)
N2—C19—C24	112.62 (8)	C44—B1—C50	112.58 (7)
N2—C19—C20	112.00 (8)	C38—B1—C50	110.28 (7)

C24—C19—C20	109.72 (9)	C44—B1—C37	105.81 (7)
N2—C19—H19	107.4	C38—B1—C37	108.83 (7)
C24—C19—H19	107.4	C50—B1—C37	107.84 (7)
C20—C19—H19	107.4	C57—C56—H56A	109.5
C19—C20—C21	111.20 (9)	C57—C56—H56B	109.5
C19—C20—H20A	109.4	H56A—C56—H56B	109.5
C21—C20—H20A	109.4	C57—C56—H56C	109.5
C19—C20—H20B	109.4	H56A—C56—H56C	109.5
C21—C20—H20B	109.4	H56B—C56—H56C	109.5
H20A—C20—H20B	108.0	C56—C57—C58	113.16 (13)
C22—C21—C20	111.37 (10)	C56—C57—H57A	108.9
C22—C21—H21A	109.4	C58—C57—H57A	108.9
C20—C21—H21A	109.4	C56—C57—H57B	108.9
C22—C21—H21B	109.4	C58—C57—H57B	108.9
C20—C21—H21B	109.4	H57A—C57—H57B	107.8
H21A—C21—H21B	108.0	C57—C58—C59	112.21 (12)
C23—C22—C21	111.18 (9)	C57—C58—H58A	109.2
C23—C22—H22A	109.4	C59—C58—H58A	109.2
C21—C22—H22A	109.4	C57—C58—H58B	109.2
C23—C22—H22B	109.4	C59—C58—H58B	109.2
C21—C22—H22B	109.4	H58A—C58—H58B	107.9
H22A—C22—H22B	108.0	C60—C59—C58	114.44 (12)
C22—C23—C24	111.10 (11)	C60—C59—H59A	108.7
C22—C23—H23A	109.4	C58—C59—H59A	108.7
C24—C23—H23A	109.4	C60—C59—H59B	108.7
C22—C23—H23B	109.4	C58—C59—H59B	108.7
C24—C23—H23B	109.4	H59A—C59—H59B	107.6
H23A—C23—H23B	108.0	C61—C60—C59	114.34 (14)
C19—C24—C23	110.70 (9)	C61—C60—H60A	108.7
C19—C24—H24A	109.5	C59—C60—H60A	108.7
C23—C24—H24A	109.5	C61—C60—H60B	108.7
C19—C24—H24B	109.5	C59—C60—H60B	108.7
C23—C24—H24B	109.5	H60A—C60—H60B	107.6
H24A—C24—H24B	108.1	C60—C61—H61A	109.5
N3—C25—C26	110.70 (7)	C60—C61—H61B	109.5
N3—C25—C30	109.76 (8)	H61A—C61—H61B	109.5
C26—C25—C30	110.12 (8)	C60—C61—H61C	109.5
N3—C25—H25	108.7	H61A—C61—H61C	109.5
C26—C25—H25	108.7	H61B—C61—H61C	109.5
C30—C25—H25	108.7		

C7—N1—C1—C2	71.61 (9)	F1—C39—C40—C41	175.29 (9)
Zr1—N1—C1—C2	−115.59 (7)	C38—C39—C40—C41	−0.11 (17)
C7—N1—C1—C6	−55.24 (10)	F2—C40—C41—F3	−1.35 (16)
Zr1—N1—C1—C6	117.56 (7)	C39—C40—C41—F3	−178.85 (10)
C7—N1—C1—Zr1	−172.80 (9)	F2—C40—C41—C42	177.96 (10)
N1—C1—C2—C3	−179.45 (8)	C39—C40—C41—C42	0.46 (16)
C6—C1—C2—C3	−51.02 (11)	F3—C41—C42—F4	−0.21 (16)

Zr1—C1—C2—C3	130.40 (7)	C40—C41—C42—F4	−179.51 (10)
C1—C2—C3—C4	53.50 (12)	F3—C41—C42—C43	178.87 (10)
C2—C3—C4—C5	−55.96 (12)	C40—C41—C42—C43	−0.43 (16)
C3—C4—C5—C6	57.56 (12)	C39—C38—C43—F5	178.13 (9)
C4—C5—C6—C1	−56.72 (12)	B1—C38—C43—F5	2.25 (15)
N1—C1—C6—C5	−179.62 (8)	C39—C38—C43—C42	0.28 (15)
C2—C1—C6—C5	52.67 (11)	B1—C38—C43—C42	−175.61 (9)
Zr1—C1—C6—C5	−128.80 (7)	F4—C42—C43—F5	1.15 (14)
C1—N1—C7—C8	−135.95 (8)	C41—C42—C43—F5	−177.93 (9)
Zr1—N1—C7—C8	55.52 (12)	F4—C42—C43—C38	179.13 (9)
C1—N1—C7—C12	98.65 (9)	C41—C42—C43—C38	0.06 (16)
Zr1—N1—C7—C12	−69.87 (12)	C49—C44—C45—F6	−177.57 (8)
N1—C7—C8—C9	−179.85 (7)	B1—C44—C45—F6	4.15 (13)
C12—C7—C8—C9	−53.68 (10)	C49—C44—C45—C46	0.88 (14)
C7—C8—C9—C10	52.04 (11)	B1—C44—C45—C46	−177.41 (9)
C8—C9—C10—C11	−54.11 (12)	F6—C45—C46—F7	−1.63 (14)
C9—C10—C11—C12	58.00 (11)	C44—C45—C46—F7	179.86 (9)
C10—C11—C12—C7	−60.66 (10)	F6—C45—C46—C47	179.28 (9)
N1—C7—C12—C11	−174.89 (7)	C44—C45—C46—C47	0.78 (16)
C8—C7—C12—C11	58.46 (10)	F7—C46—C47—F8	−0.97 (16)
C19—N2—C13—C18	−69.57 (10)	C45—C46—C47—F8	178.14 (9)
Zr1—N2—C13—C18	110.89 (7)	F7—C46—C47—C48	179.28 (9)
C19—N2—C13—C14	56.89 (10)	C45—C46—C47—C48	−1.62 (15)
Zr1—N2—C13—C14	−122.65 (7)	F8—C47—C48—F9	1.00 (16)
C19—N2—C13—Zr1	179.54 (10)	C46—C47—C48—F9	−179.25 (9)
N2—C13—C14—C15	179.54 (8)	F8—C47—C48—C49	−178.97 (9)
C18—C13—C14—C15	−52.14 (11)	C46—C47—C48—C49	0.79 (16)
Zr1—C13—C14—C15	132.36 (8)	F9—C48—C49—F10	1.77 (13)
C13—C14—C15—C16	53.20 (12)	C47—C48—C49—F10	−178.27 (9)
C14—C15—C16—C17	−54.97 (12)	F9—C48—C49—C44	−178.95 (9)
C15—C16—C17—C18	57.72 (12)	C47—C48—C49—C44	1.01 (15)
C16—C17—C18—C13	−57.44 (11)	C45—C44—C49—F10	177.47 (8)
N2—C13—C18—C17	−179.31 (7)	B1—C44—C49—F10	−4.42 (14)
C14—C13—C18—C17	53.49 (10)	C45—C44—C49—C48	−1.77 (13)
Zr1—C13—C18—C17	−130.66 (7)	B1—C44—C49—C48	176.35 (9)
C13—N2—C19—C24	129.11 (9)	C55—C50—C51—F11	−176.92 (8)
Zr1—N2—C19—C24	−51.56 (13)	B1—C50—C51—F11	5.08 (13)
C13—N2—C19—C20	−106.65 (9)	C55—C50—C51—C52	0.91 (15)
Zr1—N2—C19—C20	72.68 (12)	B1—C50—C51—C52	−177.09 (9)
N2—C19—C20—C21	177.11 (9)	F11—C51—C52—F12	−1.25 (15)
C24—C19—C20—C21	−57.05 (12)	C50—C51—C52—F12	−179.16 (10)
C19—C20—C21—C22	55.36 (13)	F11—C51—C52—C53	177.81 (10)
C20—C21—C22—C23	−54.24 (14)	C50—C51—C52—C53	−0.09 (17)
C21—C22—C23—C24	55.43 (14)	F12—C52—C53—F13	−0.21 (18)
N2—C19—C24—C23	−176.39 (9)	C51—C52—C53—F13	−179.29 (11)
C20—C19—C24—C23	58.13 (12)	F12—C52—C53—C54	178.67 (11)
C22—C23—C24—C19	−57.81 (14)	C51—C52—C53—C54	−0.40 (17)
C31—N3—C25—C26	157.72 (8)	F13—C53—C54—F14	−0.64 (18)

Zr1—N3—C25—C26	24.69 (13)	C52—C53—C54—F14	−179.52 (11)
C31—N3—C25—C30	−80.52 (11)	F13—C53—C54—C55	178.89 (10)
Zr1—N3—C25—C30	146.45 (8)	C52—C53—C54—C55	0.00 (17)
N3—C25—C26—C27	178.26 (8)	F14—C54—C55—F15	1.31 (14)
C30—C25—C26—C27	56.71 (11)	C53—C54—C55—F15	−178.22 (10)
C25—C26—C27—C28	−56.73 (12)	F14—C54—C55—C50	−179.53 (10)
C26—C27—C28—C29	55.99 (14)	C53—C54—C55—C50	0.94 (17)
C27—C28—C29—C30	−55.85 (14)	C51—C50—C55—F15	177.77 (9)
C28—C29—C30—C25	56.59 (13)	B1—C50—C55—F15	−4.41 (15)
N3—C25—C30—C29	−179.07 (9)	C51—C50—C55—C54	−1.33 (14)
C26—C25—C30—C29	−56.96 (11)	B1—C50—C55—C54	176.49 (9)
C25—N3—C31—C36	170.85 (8)	C49—C44—B1—C38	122.78 (10)
Zr1—N3—C31—C36	−39.01 (8)	C45—C44—B1—C38	−59.22 (11)
C25—N3—C31—C32	−17.46 (13)	C49—C44—B1—C50	−1.61 (13)
Zr1—N3—C31—C32	132.67 (8)	C45—C44—B1—C50	176.40 (8)
C25—N3—C31—Zr1	−150.14 (9)	C49—C44—B1—C37	−119.17 (10)
N3—C31—C32—C33	177.89 (9)	C45—C44—B1—C37	58.84 (10)
C36—C31—C32—C33	−10.78 (13)	C43—C38—B1—C44	−16.75 (13)
Zr1—C31—C32—C33	−108.10 (11)	C39—C38—B1—C44	167.68 (9)
C31—C32—C33—C34	43.52 (13)	C43—C38—B1—C50	108.93 (10)
C32—C33—C34—C35	−64.43 (12)	C39—C38—B1—C50	−66.65 (11)
C33—C34—C35—C36	50.69 (12)	C43—C38—B1—C37	−132.97 (10)
N3—C31—C36—C35	169.91 (9)	C39—C38—B1—C37	51.46 (12)
C32—C31—C36—C35	−1.82 (14)	C55—C50—B1—C44	118.60 (10)
Zr1—C31—C36—C35	136.21 (9)	C51—C50—B1—C44	−63.72 (11)
N3—C31—C36—Zr1	33.70 (7)	C55—C50—B1—C38	−6.34 (13)
C32—C31—C36—Zr1	−138.04 (8)	C51—C50—B1—C38	171.34 (8)
C34—C35—C36—C31	−18.58 (13)	C55—C50—B1—C37	−125.05 (10)
C34—C35—C36—Zr1	87.37 (11)	C51—C50—B1—C37	52.63 (11)
C43—C38—C39—F1	−175.44 (9)	Zr1—C37—B1—C44	99.6 (3)
B1—C38—C39—F1	0.68 (14)	Zr1—C37—B1—C38	−140.8 (3)
C43—C38—C39—C40	−0.25 (15)	Zr1—C37—B1—C50	−21.1 (3)
B1—C38—C39—C40	175.87 (10)	C56—C57—C58—C59	−178.95 (14)
F1—C39—C40—F2	−2.21 (15)	C57—C58—C59—C60	−169.70 (13)
C38—C39—C40—F2	−177.61 (10)	C58—C59—C60—C61	−61.46 (19)