Electronic Supplementary Information

A zwitterionic aluminabenzene-alkylzirconium complex having half-zirconocene structure: synthesis and application for additive-free ethylene polymerization

Taichi Nakamura, Katsunori Suzuki,* and Makoto Yamashita*

Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, 112-8551, Japan
Department of Molecular and Macromolecular Chemistry, Nagoya University Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

E-mail: katsuno_suzu@oec.chembio.nagoya-u.ac.jp;
makoto@oec.chembio.nagoya-u.ac.jp

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Contents

1. Experimental Procedures

General methods

All manipulations of air- and/or moisture-sensitive compounds were performed in a KOREA KIYON glove box under argon atmosphere. Anhydrous hexane and toluene were dried by passage through a Grass Contour solvent purification system. Ethylene gas was purchased from Taiyo Nippon Sanso Corporation. Deuterated benzene (C_6D_6) and deuterated toluene (Toluene-d_8) were distilled from sodium/benzophenone prior to use. Aluminacyclohexadiene[S1] and $ZrBn_4$[S2] were prepared according to the literature procedures. Other chemicals were used as received.

The nuclear magnetic resonance (NMR) measurements were carried out by a JEOL ECS-400 spectrometer (400 MHz for ^{1}H and 101 MHz for ^{13}C). Chemical shifts (δ) are given by definition as dimensionless numbers and relative to ^{1}H or ^{13}C NMR chemical shifts of the residual C_6D_5H for ^{1}H (δ = 7.16), C_6D_6 itself for ^{13}C (δ = 128.06), and C_7D_7H for ^{1}H (δ = 2.08). The absolute values of the coupling constants are given in Hertz (Hz). Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br). Elemental analyses were performed on a Perkin Elmer 2400 series II CHN analyzer. High temperature GPC measurement using 1,2-dichlorobenzene as an eluent at 145 ºC was performed on a Tosoh Corporation HLC-8321GPC/HT system calibrated by polystyrene standard. Intrinsic Viscosity measurement was performed by Mitsui Chemicals Inc. Melting points (m.p.) were determined with a MPA100 OptiMelt (Tokyo Instruments, Inc.) and are uncorrected.

Synthesis of aluminabenzene-Zr complex 3

Crystalline **4** ($0.5C_6H_{14}$) (183 mg, 0.313 mmol) was added into a toluene (3 mL) solution of $ZrBn_4$ (137 mg, 0.301 mmol). After stirring at room temperature for 100 min, the resulting red solution was concentrated under reduced pressure. The red oil was extracted with hexane and filtrated. The filtrate was cooled at –35 °C to give aluminabenzene-Zr complex **3** as red crystals (193 mg, 0.240 mmol, 80%); ^{1}H NMR (C_6D_6, 400 MHz) δ 1.07-1.18 (m, 42H), 2.01 (s, 2H), 2.16 (br, 2H), 2.29 (br, 2H), 5.40 (br t, J = 8 Hz, 1H), 6.47-7.07 (br, m, 10H), 7.22-7.25 (br, m, 5H), 7.59 (d, J = 8 Hz, 2H); Anal. calcd. for $C_{44}H_{66}AlClSi_2Zr$: C, 65.66; H8.27; N, 0.00. Found C, 65.49; H, 8.44; N, 0.05.

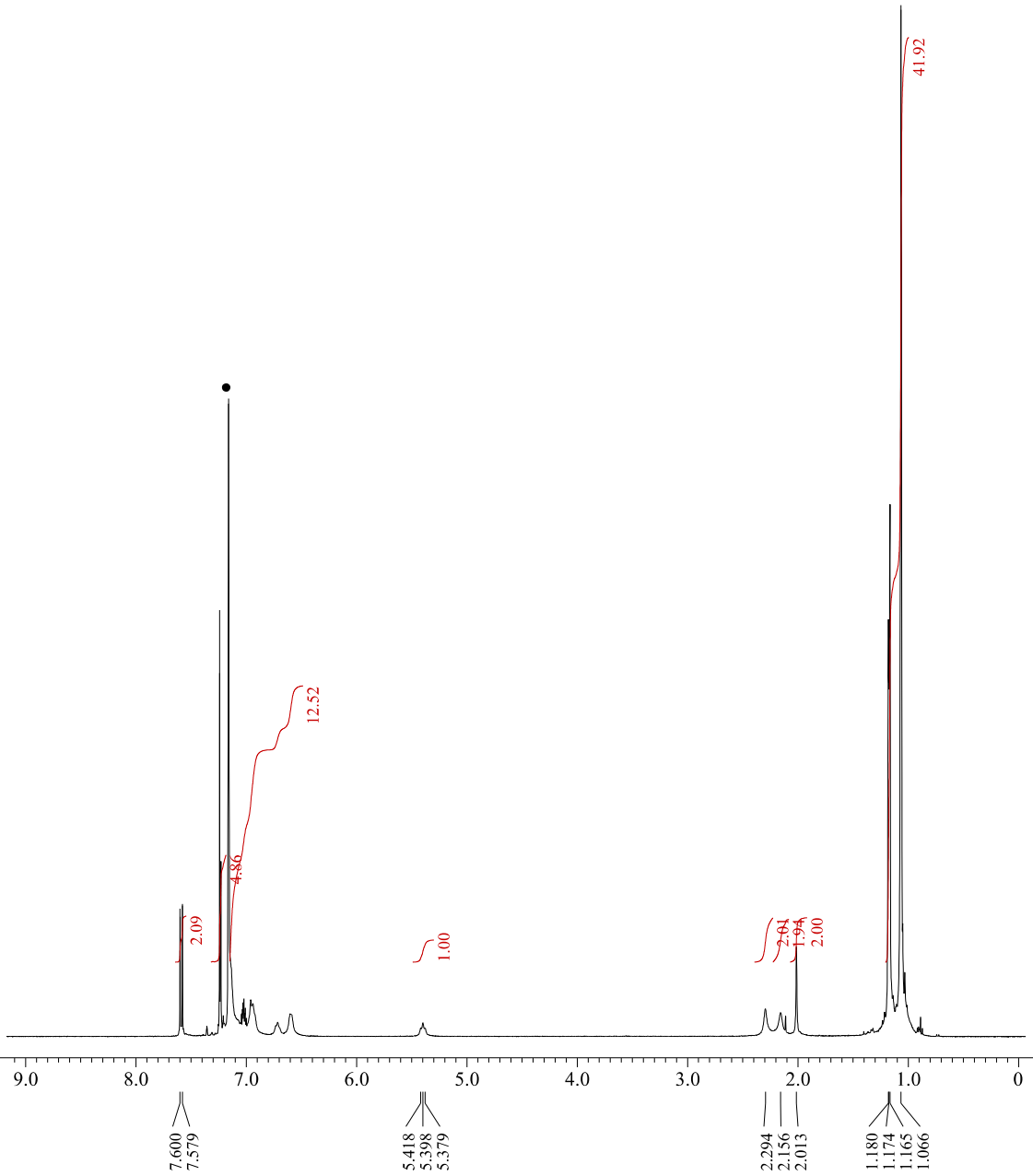


Fig. S1 ^{1}H NMR spectrum of **3** in C_6D_6. (●, residual solvent signal)

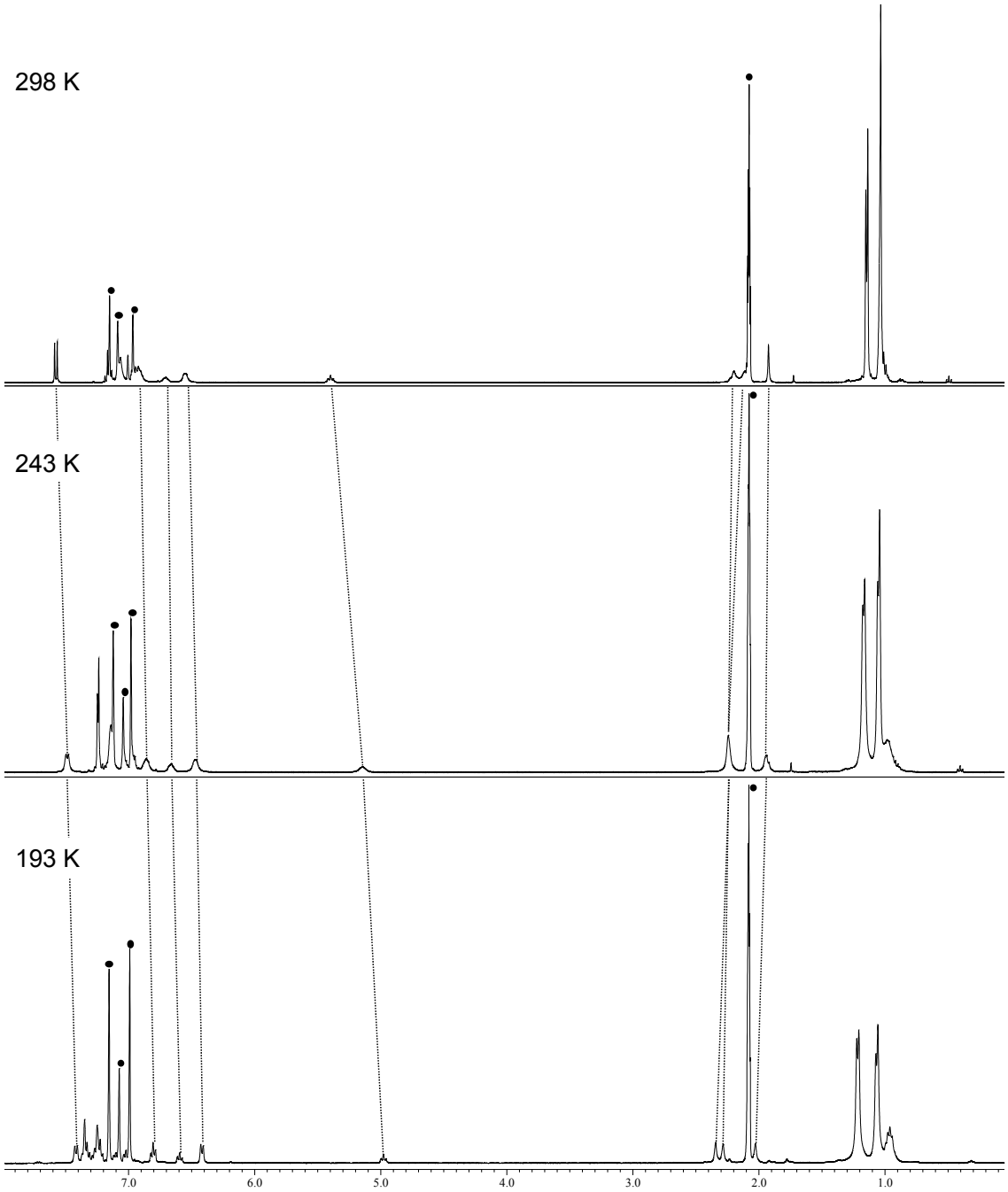
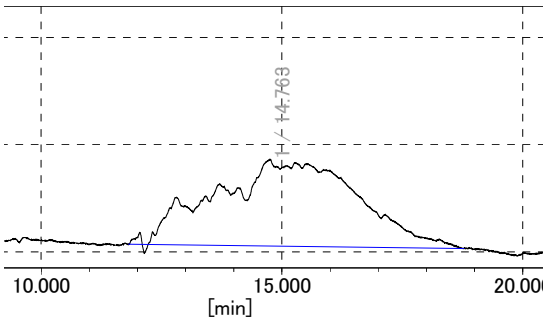


Fig. S2 Variable temperature ^{1}H NMR spectra of **3** in toluene-d_8 (•:residual solvent signal).

2. Details of Ethylene Polymerization

Experimental procedure for the catalytic ethylene polymerization

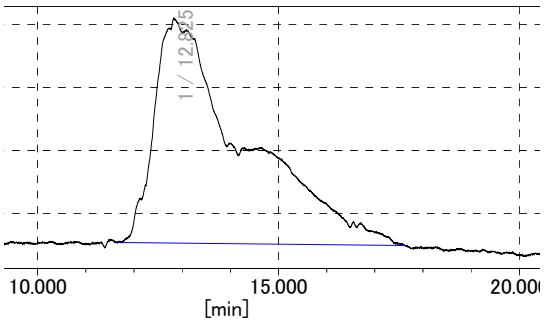
A benzene (4 ml) solution of **3** (6.4 mg, 8.0 μmol) was charged to a 300 mL autoclave at room temperature in argon filled glovebox. The autoclave was quickly pressurized with ethylene. After stirring at room temperature, MeOH was added. The resulting precipitate was collected by filtration and washed several times with HCl aq., distilled water, and MeOH. The remaining solid was dried under vacuum to afford polyethylene.



	retention time / min	molecular weight
peak start	11.817	233,335,361
peak top	14.763	845,722
peak end	18.765	20,871

M_w: 3,426,206, M_n: 328,475, M_w/M_n: 10.431

Fig. S3 GPC profile of the resulting polyethylene in entry 4, Table S1.



	retention time / min	molecular weight
peak start	11.662	391,497,290
peak top	12.825	13,620,538
peak end	17.618	67,173

M_w: 10,240,663, M_n: 1,152,042, M_w/M_n: 8.889

Fig. S4 GPC profile of the resulting polyethylene in entry 5, Table S1.

3. X-ray Crystallographic Analysis

Crystallographic data for **3** is summarized in Table S1. The crystal was coated with oil (Immersion Oil, type B: Code 1248, Cargille Laboratories, Inc.) and put on a MicroMount^{TM} (MiTeGen, LLC), and then mounted on diffractometer. Diffraction data were collected on a Rigaku Saturn CCD detectors using Mo$K\alpha$ radiation. The Bragg spots were integrated using the CrystalClear program package.[S3] Absorption corrections were applied. All the following procedure for analysis, Yadokari-XG 2009 was used as a graphical interface.[S4] The structure was solved by a direct method with programs of SIR2004[S5] and refined by a full-matrix least squares method with the program of SHELXL−2013.[S6] Anisotropic temperature factors were applied to all non-hydrogen atoms. The hydrogen atoms were put at calculated positions, and refined applying riding models. The detailed crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: Deposition code CCDC 1820642 (**3**). A copy of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/products/csd/request.

Table S1 Crystallographic data for **3**.

	3
formula	$C_{44}H_{66}AlClSi_2Zr$
M	804.79
T / K	93.2
color	red
size, mm	0.20 x 0.08 x 0.03
crystal system	Monoclinic
space group	*P*21/n(#2)
a / Å	11.2015(15)
b / Å	18.847(3)
c / Å	20.042(3)
α / °	90
β / °	90.198(2)°
γ / °	90
V / Å^3	4231.0(10)
Z	4
D_x / g cm^{-3}	1.263
μ / mm^{-1}	0.430
F(000)	1712
θ range / °	3.235 to 27.545
reflections collected	52068
unique reflections	9714
refined parameters	462
GOF on F^2	1.127
$R1$ [$I > 2\sigma(I)$][a]	0.0570
w$R2$ (all data)[b]	0.1251
$\rho_{min,\ max}$ / e Å^{-3}	-0.931, 0.727

[a] $R1 = \Sigma\ ||Fo| - |Fc|| / \Sigma\ |Fo|$, [b] $wR2 = [\Sigma\ \{w(Fo^2 - Fc^2)^2 / \Sigma\ w(Fo^2)^2\}]^{1/2}$.

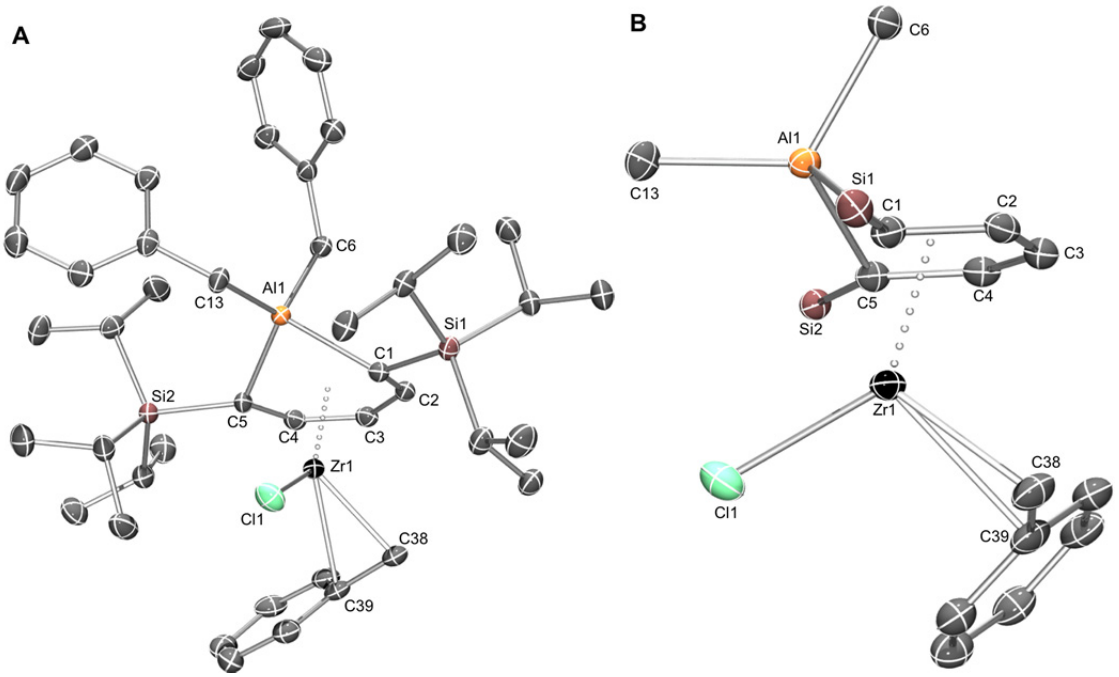


Fig. S5 (A) Molecular structure of **3** (50% thermal ellipsoid probability). Hydrogen atoms are omitted for clarity. (B) Side view of **3**. Hydrogen atoms, isopropyl groups, and Ph groups are omitted for clarity. Selected bond distances (Å) and angles (°) for **3**: Al1–C1 = 2.188(3), Al1–C5 = 2.112(3), Al1–C6 = 2.017(3), Al1–C13 = 1.993(3), C1–C2 = 1.416(4), C2–C3 = 1.423(4), C3–C4 = 1.420(4), C4–C5 = 1.407(4), Al1–Zr1 = 2.9686(9), C1–Zr1 = 2.204(3), C2–Zr1 = 2.477(3), C3–Zr1 = 2.544(3), C4–Zr1 = 2.512(3), C5–Zr1 = 2.292(3), Zr1–Cl1 = 2.3910(8), Zr1–C38 = 2.293(3), Zr1–C39 = 2.636(3), C1–Al1–C5 = 92.31(11), Al1–C1–C2 = 102.48(18), C1–C2–C3 = 127.5(3), C2–C3–C4 = 128.4(3), C3–C4–C5 = 125.7(3), C4–C5–Al1 = 107.24(19), Zr1-C38-C39 = 86.21(18).

4. Theoretical Calculations

DFT calculations were performed by using Gaussian09 program package.[S7] The geometry of **3** was optimized at the M06-L/[LanL2DZ for Zr, 6-31G(d) for Si, Al, C, H, Cl][S8-10] level of theory. The optimized structures and selected structural parameters of **3** are summarized in Fig. S6 and Table S2. The HOMO and LUMO of optimized structures of **3** is shown in Fig. S7. The Wiberg bond index (WBI)[S11] and natural population analysis (NPA)[S11] charge distribution were calculated by natural bond orbital (NBO) method (Fig. S8).[S12]

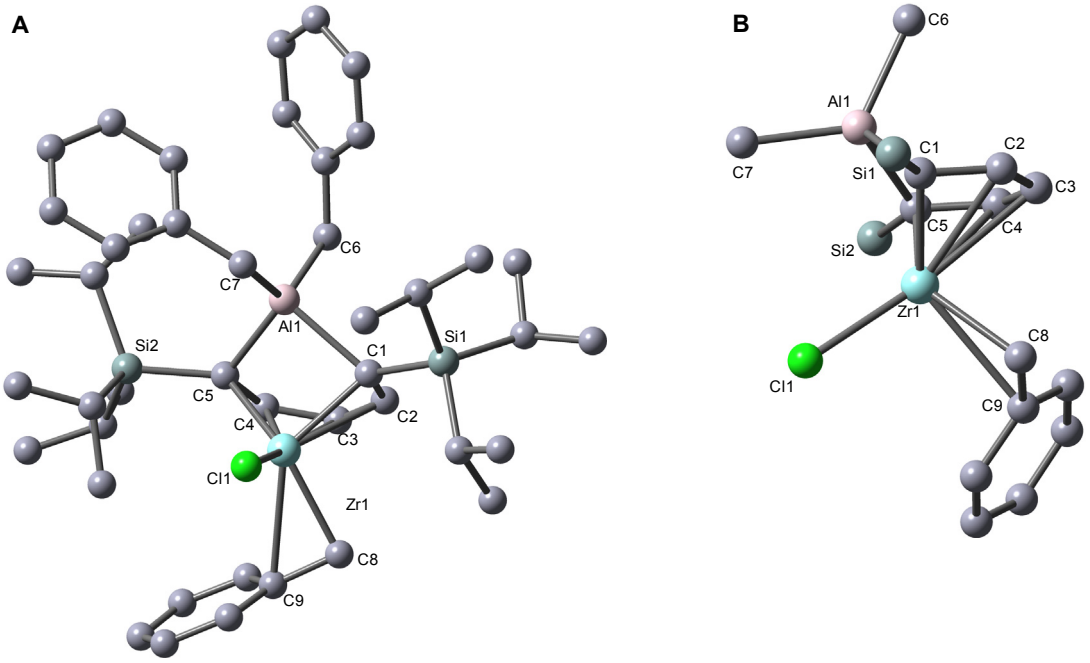


Fig. S6 (A) Optimized structure of **3** at the M06-L/[LanL2DZ for Zr, 6-31G(d) for Si, Al, Cl, C, H] level of theory. Hydrogen atoms are omitted for clarity. (B) Side view of **3**. Hydrogen atoms, Ph groups, and isopropyl groups are omitted for clarity. Selected bond distances (Å) and angles (°) for **3**: Al1–Zr1 = 2.92851, Al1–C1 = 2.19587, Al1–C5 = 2.09603, Al1–C6 = 2.01198, Al1–C7 = 1.99926, C1–C2 = 1.41483, C2–C3 = 1.41966, C3–C4 = 1.42123, C4–C5 = 1.40590, C1–Zr1 = 2.20233, C2–Zr1 = 2.52441, C3–Rh1 = 2.60493, C4–Zr1 = 2.55539, C5–Zr1 = 2.29977, C8–Zr1 = 2.30261, C9–Zr1 = 2.72015, C7–Zr1 = 3.88663, C1–Al1–C5 = 92.082, Al1–C1–C2 = 103.633, C1–C2–C3 = 127.674, C2–C3–C4 = 128.111, C3–C4–C5 = 125.523, C4–C5–Al1 =109.659, Zr1–C8–C9 = 89.654.

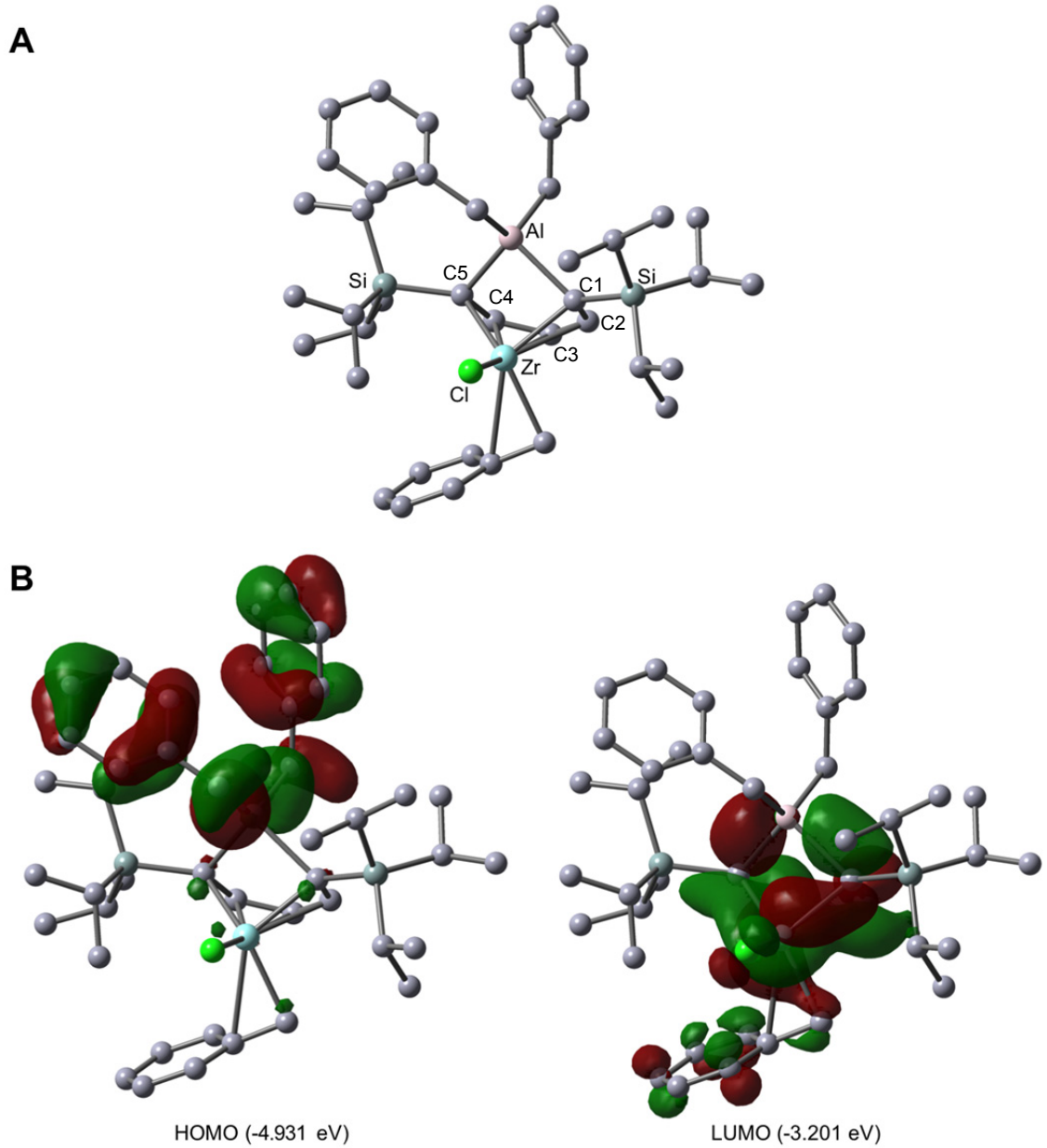


Fig. S7 (A) Optimized structure of **3**. (B) HOMO and LUMO of **3** calculated at the M06-L/[LanL2DZ for Rh, 6-31G(d) for N, Si, Al, C, H] level. Hydrogen atoms are omitted for clarity

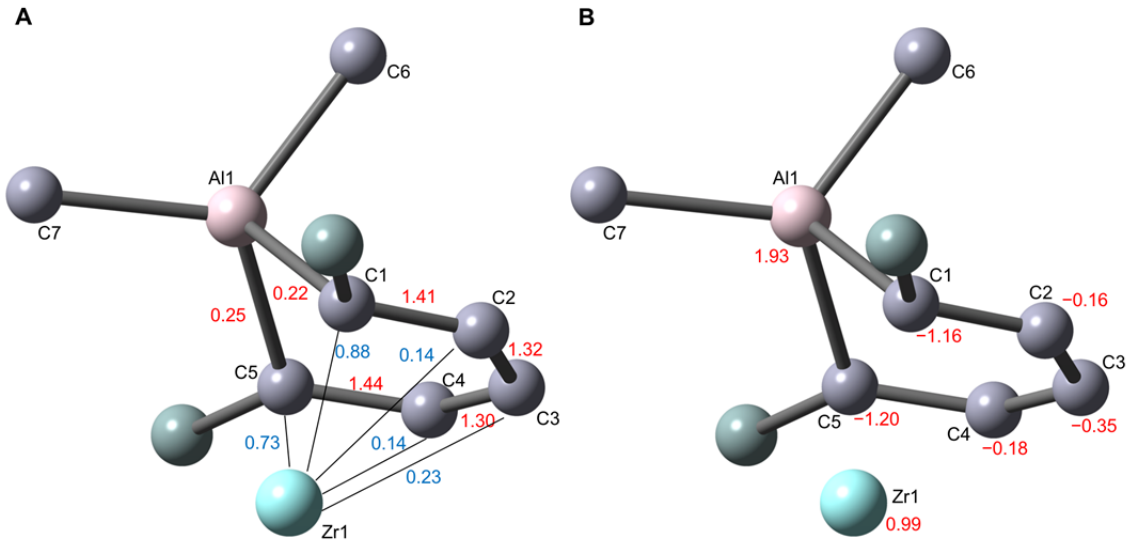


Fig. S8 (A) Wiberg bond index (red: bond order in six membered ring, blue: bond order between Zr and C). (B) Natural population analysis charge distributions.

Table S2 Cartesian coordinate of complex **3**.

Center Number	Atomic Number	Atomic Type	Coordinate (Angstroms)		
			X	Y	Z
1	6	0	1.756356	-0.873314	-0.543324
2	6	0	1.445411	-1.352372	-1.837762
3	1	0	2.222323	-1.867161	-2.420621
4	6	0	0.171708	-1.398589	-2.463051
5	1	0	0.113947	-2.004419	-3.367531
6	6	0	-1.036885	-0.783237	-2.038155
7	1	0	-1.893951	-1.026186	-2.681264
8	6	0	-1.212181	-0.067710	-0.840723
9	6	0	1.152860	2.011541	-1.970444
10	1	0	1.951391	1.412478	-2.430037
11	1	0	0.338857	2.033609	-2.709053
12	6	0	1.638705	3.390828	-1.683903
13	6	0	0.953137	4.524765	-2.143822
14	1	0	0.077462	4.388578	-2.779553
15	6	0	1.360216	5.809726	-1.794892
16	1	0	0.800020	6.669527	-2.161143
17	6	0	2.477927	5.999022	-0.986256
18	1	0	2.795014	7.002585	-0.708757
19	6	0	3.189525	4.886053	-0.540265
20	1	0	4.069793	5.016991	0.087849
21	6	0	2.772959	3.604829	-0.882992
22	1	0	3.331974	2.739318	-0.515851
23	6	0	0.613149	1.689047	1.493203
24	1	0	0.501002	0.856493	2.202849
25	1	0	1.649724	2.044113	1.617321
26	6	0	-0.330696	2.786460	1.867225
27	6	0	-0.277474	4.039048	1.234847
28	1	0	0.486126	4.220793	0.479604
29	6	0	-1.184093	5.045334	1.545610
30	1	0	-1.119247	6.000725	1.024272
31	6	0	-2.168448	4.836655	2.511551
32	1	0	-2.882571	5.622480	2.752480
33	6	0	-2.214178	3.613439	3.176224
34	1	0	-2.961943	3.438662	3.949691
35	6	0	-1.306304	2.604742	2.859133
36	1	0	-1.350830	1.651814	3.390362
37	6	0	3.186856	-0.140521	2.728219
38	1	0	3.672855	-0.971573	3.255713
39	1	0	2.140334	-0.429775	2.583217
40	1	0	3.197020	0.722897	3.407915
41	6	0	3.910749	0.172882	1.417923
42	1	0	3.490119	1.113290	1.016940
43	6	0	5.393944	0.426579	1.685477
44	1	0	5.521844	1.174502	2.480983
45	1	0	5.925180	0.800001	0.801665
46	1	0	5.910972	-0.483789	2.019434
47	6	0	4.774981	0.446316	-1.963657
48	1	0	5.202682	1.150678	-1.236416

Table S2 Cartesian coordinate of complex **3** (continued).

Center Number	Atomic Number	Atomic Type	Coordinate (Angstroms)		
			X	Y	Z
49	1	0	3.782084	0.827486	-2.232447
50	1	0	5.400822	0.502914	-2.865525
51	6	0	4.724450	-0.975219	-1.408494
52	1	0	4.293168	-1.621596	-2.193743
53	6	0	6.141596	-1.494091	-1.153613
54	1	0	6.759113	-1.391386	-2.057598
55	1	0	6.158529	-2.552529	-0.869803
56	1	0	6.650940	-0.937309	-0.357133
57	6	0	4.781470	-3.207803	1.705735
58	1	0	4.741028	-4.244513	2.069980
59	1	0	4.790213	-2.556212	2.587167
60	1	0	5.750102	-3.086576	1.202927
61	6	0	3.610864	-2.912912	0.767809
62	1	0	2.680382	-3.036190	1.353315
63	6	0	3.578090	-3.931419	-0.372427
64	1	0	4.518006	-3.926902	-0.940844
65	1	0	2.766557	-3.738539	-1.086254
66	1	0	3.439330	-4.954458	0.005901
67	6	0	-2.254054	3.181105	-1.427349
68	1	0	-2.533331	2.865935	-2.444266
69	1	0	-1.179822	2.996498	-1.307728
70	1	0	-2.387451	4.272222	-1.372952
71	6	0	-3.069602	2.478099	-0.348828
72	1	0	-2.646375	2.781933	0.620536
73	6	0	-4.518438	2.969759	-0.364999
74	1	0	-4.552955	4.054095	-0.183344
75	1	0	-5.140234	2.493262	0.403079
76	1	0	-5.004465	2.793677	-1.334464
77	6	0	-4.218860	0.663154	2.260664
78	1	0	-5.231590	0.521031	1.856466
79	1	0	-4.027471	1.741995	2.312541
80	1	0	-4.230800	0.284095	3.293432
81	6	0	-3.169700	-0.060542	1.422524
82	1	0	-2.184474	0.139625	1.885952
83	6	0	-3.392769	-1.567681	1.457356
84	1	0	-3.197857	-2.000003	2.448371
85	1	0	-2.750763	-2.114581	0.745584
86	1	0	-4.421186	-1.830539	1.175990
87	6	0	-4.161862	0.419993	-2.957595
88	1	0	-4.755138	-0.165976	-3.675337
89	1	0	-3.154940	0.535101	-3.379564
90	1	0	-4.605159	1.424111	-2.928659
91	6	0	-4.171751	-0.226133	-1.569387
92	1	0	-3.807368	-1.264252	-1.675700
93	6	0	-5.608514	-0.311851	-1.054124
94	1	0	-6.050423	0.683463	-0.915400
95	1	0	-5.681998	-0.836821	-0.094257
96	1	0	-6.251349	-0.849035	-1.768087

Table S2 Cartesian coordinate of complex **3** (continued).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
97	13	0	0.554280	0.955710	-0.365771
98	14	0	3.538057	-1.129350	0.083006
99	14	0	-2.933334	0.578649	-0.357574
100	6	0	0.149213	-4.032925	-0.633999
101	1	0	0.560801	-4.151437	-1.638403
102	6	0	-1.296737	-4.227452	-0.537663
103	6	0	-1.902550	-4.677574	0.660595
104	1	0	-1.262303	-4.946151	1.500877
105	6	0	-3.279589	-4.805379	0.765215
106	1	0	-3.714064	-5.176978	1.691785
107	6	0	-4.108814	-4.449969	-0.301070
108	1	0	-5.189225	-4.544334	-0.211742
109	6	0	-3.541832	-3.969824	-1.477882
110	1	0	-4.178261	-3.693997	-2.318030
111	6	0	-2.158716	-3.854974	-1.597861
112	1	0	-1.720520	-3.538231	-2.544110
113	40	0	-0.109177	-1.860797	0.085106
114	17	0	-0.050338	-2.141001	2.486773
115	1	0	0.728689	-4.588326	0.112389

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