Supporting Information

Title: Synthesis, structure and reactions of triarylgermyl anion with α,δ-ambiphilic character

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1. Experimental Details.

Generals. ^{1}H (400 MHz), ^{13}C{^{1}H} (100 MHz), ^{19}F{^{1}H} (376 MHz), and ^{29}Si{^{1}H} (79.4 MHz) NMR spectra were recorded with a JEOL EX-400 or AL-400 spectrometer. ^{1}H chemical shifts in C_6D_6 were referenced to the residual proton ($\delta(^{1}H) = 7.20$). ^{13}C chemical shifts were referenced to internal C_6D_6 ($\delta = 128.0$) or external tetramethylsilane ($\delta = 0$). ^{19}F chemical shifts were referenced to external $CFCl_3$ ($\delta = 0$). ^{29}Si chemical shifts were referenced to external tetramethylsilane ($\delta = 0$). NMR spectra in THP were observed in an unlocked mode, being referenced to a standard substance in THP-THF-d_8 (4:1 v/v) that was observed in a locked mode. The mass spectra (EI) were measured at 70 eV with a JEOL SX-102A mass spectrometer at the Natural Science Center for Basic Research and Development (N-BARD), Hiroshima University: we thank Dr. Daisuke Kajiya for the measurement of the samples. Melting points were measured with a Yanaco micro melting point apparatus and were uncorrected. The elemental analyses were performed using Perkin-Elmer 2400CHN elemental analyzer at our laboratory.

KF (spray dried grade (98%) was purchased from Wako Pure Chemical Industries, Ltd. and dried in vacuo at 100 °C overnight. $LiBPh_4$•3dme was purchased from Alfa Aesar and dried in vacuo at 140 °C overnight using P_2O_5 as desiccant. BF_3•Et_2O was distilled under nitrogen atmosphere over CaH_2. [2.2.2]Cryptand (Wako Pure Chemical Industries, Ltd.) was used as received. CH_3COOH was distilled under nitrogen atmosphere. Hexane was distilled under nitrogen atmosphere over calcium hydride or dehydrated solvent (<10 ppm; Kanto Chemical Co., Inc.) was dried through Solvent Dispensing System (GlassContour) under nitrogen atmosphere (99.999%). THP (tetrahydropyran) and THF-d_8 were distilled under nitrogen atmosphere over sodium diphenylketyl. All reactions were carried out under inert gas atmosphere.

Reaction of 1 with KF/[2.2.2]cryptand:

Potassium [2.2.2]cryptand tris[2-(fluorodimethylsilyl)phenyl]germanide (3).

To **2** (770 mg, 1.50 mmol), KF (89 mg, 1.50 mmol) and [2.2.2]cryptand (565 mg, 1.50 mmol) in a schlenk tube was added THP (5.0 mL) at room temperature. The reaction mixture was stirred at room temperature for 0.5 h to give a yellow solution of **3**. The reaction mixture was concentrated in vacuo. The resulting yellow solid was recrystallized from THP-hexane (5 mL/5 mL) at –30 °C to give **3** (1.10 g, 77% yield) as yellow crystals.

Mp: 62 °C (decomposed) (in a sealed tube). ^{13}C{^{1}H} NMR (THP, δ): 0.98 (br, Si*Me*$_2$F), 52.54 (cryptand), 66.21 (cryptand), 69.06 (cryptand), 121.25 (CH), 125.95 (CH), 130.80 (CH), 135.90 (CH), 143.41 (d, $^{2}J(^{13}C\text{-}^{19}F) = 14$ Hz, *C*-Si), 168.90 (d, $^{3}J(^{13}C\text{-}^{19}F) = 6$ Hz, *C*-Ge). ^{19}F{^{1}H} NMR

(THP δ): –161.20 (s). ^{29}Si{^{1}H} NMR (THP, δ): 15.52 (d, ^{1}J(^{29}Si-^{19}F) = 274 Hz).

Reaction of 2 with CH_3COOH: Tris[2-(fluorodimethylsilyl)phenyl]germane (4).

To **2** (154 mg, 0.30 mmol) and KF (18 mg, 0.30 mmol) in a schlenk tube was added THP (1.0 mL) at room temperature. The reaction mixture was stirred at room temperature for 0.5 h to give a yellow solution of **3**. CH_3COOH (40 μL, 0.70 mmol) was added to the solution of **1** at 0 °C, and the reaction mixture was stirred at that temperature for 10 min to yield **4**. The reaction mixture was concentrated in vacuo. Hexane (5 mL x 3) was added to the residue and the resulting insoluble materials were filtered off. The filtrate was concentrated in vacuo. The residue was recrystallized from hexane at –30 °C to give **4** (100 mg, 62% yield) as white solids.

Mp: 93.0–95.0 °C. ^{1}H NMR (C_6D_6, δ): 0.39 (d, ^{3}J(^{19}F-^{1}H) = 8 Hz, 18H), 6.81 (q, ^{5}J(^{19}F-^{1}H) = 8 Hz, 1H, Ge-*H*), 7.05 (ddd, *J* = 8, 8, and 1 Hz, 3H), 7.16 (m, 1H), 7.45 (d, *J* = 8 Hz, 1H), 7.67 (dd, *J* = 8 and 1 Hz, 1H). ^{13}C{^{1}H} NMR (C_6D_6, δ): 0.62 (d, ^{2}J(^{13}C-^{19}F) = 15 Hz, Si*Me*$_2$F), 128.47 (CH), 129.61 (CH), 134.90 (d, ^{3}J(^{13}C-^{19}F) = 6 Hz, CH), 137.05 (CH), 143.29 (*C*-Ge), 143.69 (d, ^{2}J(^{13}C-^{19}F) = 15 Hz, *C*-Si). ^{13}C{^{1}H} NMR (THP, δ): 0.65 (d, ^{2}J(^{13}C-^{19}F) = 15 Hz, Si*Me*$_2$F), 128.71 (CH), 129.80 (CH), 135.11 (d, ^{3}J(^{13}C-^{19}F) = 5 Hz, CH), 137.18 (CH), 143.32 (*C*-Ge), 143.92 (d, ^{2}J(^{13}C-^{19}F) = 15 Hz, *C*-Si). ^{19}F{^{1}H} NMR (C_6D_6, δ): –156.10 (sept, ^{3}J(^{19}F-^{1}H) = 8 Hz). ^{19}F{^{1}H} NMR (THP δ): –155.4 (broad). ^{29}Si{^{1}H} NMR (C_6D_6, δ): 20.97 (d, ^{1}J(^{29}Si-^{19}F) = 280 Hz). ^{29}Si{^{1}H} NMR (THP, δ): 20.13 (d, ^{1}J(^{29}Si-^{19}F) = 280 Hz). MS (EI): *m/z* 533 {M$^+$(for ^{74}Ge) – [H], 0.7}, 531 {M$^+$(for ^{72}Ge) – [H], 0.5}, 530 {M$^+$(for ^{70}Ge) – [H], 0.2}, 381 {M$^+$(for ^{74}Ge) – [(C_6H_4)SiMe_2F], 100}, 379 {M$^+$(for ^{72}Ge) – [(C_6H_4)SiMe_2F], 79}, 377 {M$^+$(for ^{70}Ge) – [(C_6H_4)SiMe_2F], 51}. Anal. Calcd for $C_{24}H_{31}F_3GeSi_3$: C, 54.05; H, 5.86. Found: C, 54.30; H, 5.77.

Reaction of 1 with $LiBPh_4$•3dme: Formation of 2.

To **3** (190 mg, 0.20 mmol) and $LiBPh_4$•3dme (357 mg, 0.60 mmol) in a schlenk tube was added THP (5.0 mL) at room temperature. The reaction mixture was stirred at the same temperature for 20 h. The formed inorganic salts were removed by filtration through a filter paper. The filtrate was concentrated in vacuo. Hexane (6 mL) was added to the residue and the resulting insoluble materials were filtered off using a membrane filter. The filtrate was concentrated in vacuo. The residue was recrystallized from hexane at –30 °C to give **2** (62 mg, 60% yield) as colorless crystals.

Reaction of 1 with BF_3•Et_2O: Formation of 2.

To **3** (190 mg, 0.20 mmol) in THP (4.0 mL) was added BF_3•Et_2O (27 μL, 0.22 mmol) at room temperature and the reaction mixture was stirred at the same temperature for 0.5 h. The formed inorganic salts were removed by filtration through a membrane filter. The filtrate was concentrated in vacuo. Hexane (3 mL x 3) was added to the residue and the resulting insoluble materials were filtered off by a filter paper. The filtrate was concentrated in vacuo. The residue

was recrystallized from hexane at –30 °C to give **2** (40 mg, 39% yield) as colorless crystals.

2. Crystallographic Data for 3.

X-ray crystallographic data for compound **3** were collected with a SCXmini (Rigaku) CCD diffractometer with a graphite monochromated Mo-*K*α radiation (λ = 0.71073 Å) at 173 K. The data were processed by using CrystalClear. The structure was solved by direct methods using SIR 97[1] and refined by a full-matrix least-squares procedure based on F^2 with SHELX-97.[2] All non-hydrogen atoms were refined anisotropically while all hydrogen atoms were located at the expected positions by a geometrical calculation and refined isotropically. The details are summarized in Tables S-1 - S-6.

Table S-1. Crystal data and structure refinement for **3**.

Identification code	(Triarylgermyl)potassium **3**	
Empirical formula	C42 H66 F3 Ge K N2 O6 Si3	
Formula weight	947.93	
Temperature	173(2) K	
Wavelength	0.71075 Å	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.5904(9) Å	α = 77.929(2)°.
	b = 13.6336(10) Å	β = 83.078(2)°.
	c = 16.5928(12) Å	γ = 71.543(2)°.
Volume	2427.9(3) $Å^3$	
Z	2	
Density (calculated)	1.297 Mg/m^3	
Absorption coefficient	0.846 mm^{-1}	
F(000)	1000	
Crystal size	0.40 x 0.40 x 0.30 mm^3	
Theta range for data collection	3.04 to 27.48°.	
Index ranges	-14<=h<=15, -17<=k<=17, -21<=l<=21	
Reflections collected	24640	
Independent reflections	11047 [R(int) = 0.0339]	
Completeness to theta = 27.48°	99.2 %	
Max. and min. transmission	0.7854 and 0.6770	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11047 / 0 / 529	
Goodness-of-fit on F^2	1.039	
Final R indices [I>2sigma(I)]	R1 = 0.0449, wR2 = 0.0982	
R indices (all data)	R1 = 0.0624, wR2 = 0.1069	
Largest diff. peak and hole	0.541 and -0.473 $e.Å^{-3}$	

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

	x	y	z	U(eq)
Ge(1)	635(1)	2983(1)	7775(1)	27(1)
Si(1)	869(1)	1498(1)	6305(1)	34(1)
Si(2)	3370(1)	2915(1)	8405(1)	36(1)
Si(3)	-486(1)	5555(1)	6734(1)	34(1)
F(1)	599(2)	817(1)	5698(1)	57(1)
F(2)	4547(2)	2690(2)	8930(1)	63(1)
F(3)	-1144(2)	6814(1)	6518(1)	52(1)
C(1)	-663(2)	2330(2)	7655(2)	28(1)
C(2)	-510(2)	1735(2)	7028(2)	30(1)
C(3)	-1411(2)	1273(2)	6963(2)	43(1)
C(4)	-2438(3)	1398(2)	7484(2)	51(1)
C(5)	-2605(2)	1984(2)	8093(2)	46(1)
C(6)	-1726(2)	2445(2)	8172(2)	36(1)
C(7)	1120(3)	2656(2)	5593(2)	52(1)
C(8)	2245(2)	631(2)	6828(2)	42(1)
C(9)	1395(2)	1996(2)	8792(1)	30(1)
C(10)	2516(2)	2029(2)	9021(2)	34(1)
C(11)	3034(3)	1361(2)	9734(2)	47(1)
C(12)	2478(3)	672(2)	10222(2)	49(1)
C(13)	1394(3)	621(2)	9998(2)	43(1)
C(14)	871(2)	1270(2)	9292(2)	37(1)
C(15)	4011(3)	2578(2)	7385(2)	45(1)
C(16)	2599(3)	4339(2)	8354(2)	48(1)
C(17)	-377(2)	4195(2)	8331(1)	30(1)
C(18)	-733(2)	5234(2)	7877(2)	32(1)
C(19)	-1316(3)	6069(2)	8296(2)	44(1)
C(20)	-1547(3)	5902(3)	9139(2)	54(1)
C(21)	-1213(3)	4894(2)	9578(2)	52(1)
C(22)	-640(3)	4061(2)	9179(2)	42(1)
C(23)	1101(3)	5397(2)	6307(2)	43(1)
C(24)	-1330(3)	4980(2)	6182(2)	41(1)
K(1)	3953(1)	7573(1)	7168(1)	35(1)
N(1)	4410(3)	7436(2)	5348(2)	57(1)
N(2)	3537(3)	7711(2)	8970(2)	61(1)
O(1)	2000(2)	7784(2)	6243(2)	60(1)
O(2)	1551(2)	8128(2)	7876(2)	56(1)
O(3)	5521(2)	5715(1)	6630(1)	42(1)
O(4)	4910(2)	5768(2)	8313(1)	58(1)
O(5)	5256(2)	8869(2)	6117(1)	50(1)
O(6)	5055(2)	8738(2)	7848(1)	52(1)
C(25)	3269(4)	7438(4)	5035(3)	87(1)
C(26)	2140(4)	8161(4)	5385(3)	90(2)
C(27)	811(3)	8269(3)	6578(3)	71(1)
C(28)	719(3)	7850(3)	7463(3)	75(1)
C(29)	1406(4)	7841(3)	8745(2)	79(1)
C(30)	2227(4)	8219(3)	9136(2)	70(1)
C(31)	5377(3)	6475(3)	5219(2)	61(1)
C(32)	5309(3)	5547(3)	5855(2)	58(1)
C(33)	5683(3)	4789(2)	7240(2)	59(1)
C(34)	5944(3)	5009(2)	8028(2)	65(1)
C(35)	5110(5)	5969(3)	9088(2)	102(2)
C(36)	3918(5)	6623(3)	9432(2)	103(2)
C(37)	4769(4)	8368(3)	4940(2)	83(1)
C(38)	5744(4)	8540(3)	5366(2)	77(1)
C(39)	6174(3)	8948(3)	6580(3)	67(1)
C(40)	5588(3)	9428(3)	7312(2)	63(1)
C(41)	4401(3)	9174(3)	8545(2)	64(1)
C(42)	4261(4)	8303(3)	9203(2)	78(1)

Table S-3. Bond lengths [Å] and angles [°] for **3**.

Ge(1)-C(1)	2.023(2)
Ge(1)-C(9)	2.024(2)
Ge(1)-C(17)	2.027(2)
Si(1)-F(1)	1.6206(17)
Si(1)-C(8)	1.844(3)
Si(1)-C(7)	1.844(3)
Si(1)-C(2)	1.864(3)
Si(2)-F(2)	1.6194(17)
Si(2)-C(16)	1.851(3)
Si(2)-C(15)	1.853(3)
Si(2)-C(10)	1.866(3)
Si(3)-F(3)	1.6232(17)
Si(3)-C(24)	1.848(3)
Si(3)-C(23)	1.852(3)
Si(3)-C(18)	1.863(3)
C(1)-C(6)	1.399(3)
C(1)-C(2)	1.409(3)
C(2)-C(3)	1.404(3)
C(3)-C(4)	1.370(4)
C(3)-H(3A)	0.9500
C(4)-C(5)	1.374(4)
C(4)-H(4A)	0.9500
C(5)-C(6)	1.386(4)
C(5)-H(5A)	0.9500
C(6)-H(6A)	0.9500
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-C(14)	1.398(3)
C(9)-C(10)	1.413(3)
C(10)-C(11)	1.402(4)
C(11)-C(12)	1.376(4)
C(11)-H(11A)	0.9500
C(12)-C(13)	1.378(4)
C(12)-H(12A)	0.9500
C(13)-C(14)	1.386(4)
C(13)-H(13A)	0.9500
C(14)-H(14A)	0.9500
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-C(22)	1.390(3)
C(17)-C(18)	1.415(3)
C(18)-C(19)	1.402(4)
C(19)-C(20)	1.376(4)
C(19)-H(19A)	0.9500
C(20)-C(21)	1.371(4)
C(20)-H(20A)	0.9500
C(21)-C(22)	1.379(4)
C(21)-H(21A)	0.9500
C(22)-H(22A)	0.9500
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
K(1)-O(4)	2.778(2)
K(1)-O(1)	2.793(2)
K(1)-O(6)	2.795(2)
K(1)-O(2)	2.820(2)
K(1)-O(3)	2.8553(19)
K(1)-O(5)	2.866(2)
K(1)-N(2)	3.007(3)
K(1)-N(1)	3.036(3)
N(1)-C(31)	1.466(4)
N(1)-C(37)	1.468(5)
N(1)-C(25)	1.476(5)
N(2)-C(42)	1.463(5)
N(2)-C(36)	1.474(4)
N(2)-C(30)	1.475(5)
O(1)-C(26)	1.418(5)
O(1)-C(27)	1.427(4)
O(2)-C(29)	1.417(4)
O(2)-C(28)	1.429(4)
O(3)-C(32)	1.416(4)
O(3)-C(33)	1.419(3)
O(4)-C(34)	1.420(4)
O(4)-C(35)	1.429(5)
O(5)-C(38)	1.406(4)
O(5)-C(39)	1.428(4)
O(6)-C(40)	1.393(4)
O(6)-C(41)	1.434(4)
C(25)-C(26)	1.503(5)
C(25)-H(25A)	0.9900
C(25)-H(25B)	0.9900
C(26)-H(26A)	0.9900
C(26)-H(26B)	0.9900
C(27)-C(28)	1.465(6)
C(27)-H(27A)	0.9900
C(27)-H(27B)	0.9900
C(28)-H(28A)	0.9900
C(28)-H(28B)	0.9900
C(29)-C(30)	1.480(6)
C(29)-H(29A)	0.9900
C(29)-H(29B)	0.9900
C(30)-H(30A)	0.9900
C(30)-H(30B)	0.9900
C(31)-C(32)	1.485(5)
C(31)-H(31A)	0.9900
C(31)-H(31B)	0.9900
C(32)-H(32A)	0.9900
C(32)-H(32B)	0.9900
C(33)-C(34)	1.485(5)
C(33)-H(33A)	0.9900
C(33)-H(33B)	0.9900
C(34)-H(34A)	0.9900
C(34)-H(34B)	0.9900
C(35)-C(36)	1.507(6)
C(35)-H(35A)	0.9900
C(35)-H(35B)	0.9900
C(36)-H(36A)	0.9900
C(36)-H(36B)	0.9900
C(37)-C(38)	1.504(6)
C(37)-H(37A)	0.9900
C(37)-H(37B)	0.9900
C(38)-H(38A)	0.9900
C(38)-H(38B)	0.9900

C(39)-C(40)	1.488(5)
C(39)-H(39A)	0.9900
C(39)-H(39B)	0.9900
C(40)-H(40A)	0.9900
C(40)-H(40B)	0.9900
C(41)-C(42)	1.471(5)
C(41)-H(41A)	0.9900
C(41)-H(41B)	0.9900
C(42)-H(42A)	0.9900
C(42)-H(42B)	0.9900
C(1)-Ge(1)-C(9)	99.23(9)
C(1)-Ge(1)-C(17)	100.23(9)
C(9)-Ge(1)-C(17)	97.78(9)
F(1)-Si(1)-C(8)	104.96(11)
F(1)-Si(1)-C(7)	103.60(13)
C(8)-Si(1)-C(7)	113.53(14)
F(1)-Si(1)-C(2)	103.86(11)
C(8)-Si(1)-C(2)	112.31(12)
C(7)-Si(1)-C(2)	116.88(12)
F(2)-Si(2)-C(16)	103.75(12)
F(2)-Si(2)-C(15)	104.77(12)
C(16)-Si(2)-C(15)	112.86(14)
F(2)-Si(2)-C(10)	104.08(11)
C(16)-Si(2)-C(10)	115.33(12)
C(15)-Si(2)-C(10)	114.39(12)
F(3)-Si(3)-C(24)	104.61(11)
F(3)-Si(3)-C(23)	103.84(11)
C(24)-Si(3)-C(23)	112.90(13)
F(3)-Si(3)-C(18)	103.63(10)
C(24)-Si(3)-C(18)	112.65(12)
C(23)-Si(3)-C(18)	117.42(12)
C(6)-C(1)-C(2)	117.8(2)
C(6)-C(1)-Ge(1)	122.55(19)
C(2)-C(1)-Ge(1)	119.65(17)
C(3)-C(2)-C(1)	118.9(2)
C(3)-C(2)-Si(1)	118.6(2)
C(1)-C(2)-Si(1)	122.53(18)
C(4)-C(3)-C(2)	121.7(3)
C(4)-C(3)-H(3A)	119.2
C(2)-C(3)-H(3A)	119.2
C(3)-C(4)-C(5)	120.1(3)
C(3)-C(4)-H(4A)	119.9
C(5)-C(4)-H(4A)	119.9
C(4)-C(5)-C(6)	119.3(3)
C(4)-C(5)-H(5A)	120.4
C(6)-C(5)-H(5A)	120.4
C(5)-C(6)-C(1)	122.2(3)
C(5)-C(6)-H(6A)	118.9
C(1)-C(6)-H(6A)	118.9
Si(1)-C(7)-H(7A)	109.5
Si(1)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
Si(1)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
Si(1)-C(8)-H(8A)	109.5
Si(1)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
Si(1)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(14)-C(9)-C(10)	117.2(2)
C(14)-C(9)-Ge(1)	123.50(18)
C(10)-C(9)-Ge(1)	119.28(18)
C(11)-C(10)-C(9)	119.5(2)
C(11)-C(10)-Si(2)	117.58(19)
C(9)-C(10)-Si(2)	122.94(19)
C(12)-C(11)-C(10)	121.7(3)
C(12)-C(11)-H(11A)	119.2
C(10)-C(11)-H(11A)	119.2
C(11)-C(12)-C(13)	119.4(3)
C(11)-C(12)-H(12A)	120.3
C(13)-C(12)-H(12A)	120.3
C(12)-C(13)-C(14)	119.8(3)
C(12)-C(13)-H(13A)	120.1
C(14)-C(13)-H(13A)	120.1
C(13)-C(14)-C(9)	122.4(2)
C(13)-C(14)-H(14A)	118.8
C(9)-C(14)-H(14A)	118.8
Si(2)-C(15)-H(15A)	109.5
Si(2)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
Si(2)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
Si(2)-C(16)-H(16A)	109.5
Si(2)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
Si(2)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(22)-C(17)-C(18)	117.3(2)
C(22)-C(17)-Ge(1)	121.72(19)
C(18)-C(17)-Ge(1)	120.63(17)
C(19)-C(18)-C(17)	119.2(2)
C(19)-C(18)-Si(3)	117.7(2)
C(17)-C(18)-Si(3)	123.09(18)
C(20)-C(19)-C(18)	121.5(3)
C(20)-C(19)-H(19A)	119.2
C(18)-C(19)-H(19A)	119.2
C(21)-C(20)-C(19)	119.3(3)
C(21)-C(20)-H(20A)	120.4
C(19)-C(20)-H(20A)	120.4
C(20)-C(21)-C(22)	120.2(3)
C(20)-C(21)-H(21A)	119.9
C(22)-C(21)-H(21A)	119.9
C(21)-C(22)-C(17)	122.4(3)
C(21)-C(22)-H(22A)	118.8
C(17)-C(22)-H(22A)	118.8
Si(3)-C(23)-H(23A)	109.5
Si(3)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
Si(3)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
Si(3)-C(24)-H(24A)	109.5
Si(3)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
Si(3)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
O(4)-K(1)-O(1)	121.82(7)
O(4)-K(1)-O(6)	92.15(7)
O(1)-K(1)-O(6)	142.24(6)
O(4)-K(1)-O(2)	97.81(7)

O(1)-K(1)-O(2)	59.96(7)	O(1)-C(26)-H(26B)	109.9
O(6)-K(1)-O(2)	102.81(7)	C(25)-C(26)-H(26B)	109.9
O(4)-K(1)-O(3)	59.75(6)	H(26A)-C(26)-H(26B)	108.3
O(1)-K(1)-O(3)	95.97(6)	O(1)-C(27)-C(28)	109.5(3)
O(6)-K(1)-O(3)	116.85(6)	O(1)-C(27)-H(27A)	109.8
O(2)-K(1)-O(3)	133.70(6)	C(28)-C(27)-H(27A)	109.8
O(4)-K(1)-O(5)	127.37(7)	O(1)-C(27)-H(27B)	109.8
O(1)-K(1)-O(5)	103.28(7)	C(28)-C(27)-H(27B)	109.8
O(6)-K(1)-O(5)	59.89(6)	H(27A)-C(27)-H(27B)	108.2
O(2)-K(1)-O(5)	129.62(6)	O(2)-C(28)-C(27)	109.4(3)
O(3)-K(1)-O(5)	92.27(6)	O(2)-C(28)-H(28A)	109.8
O(4)-K(1)-N(2)	61.75(7)	C(27)-C(28)-H(28A)	109.8
O(1)-K(1)-N(2)	120.23(8)	O(2)-C(28)-H(28B)	109.8
O(6)-K(1)-N(2)	59.03(8)	C(27)-C(28)-H(28B)	109.8
O(2)-K(1)-N(2)	60.58(8)	H(28A)-C(28)-H(28B)	108.2
O(3)-K(1)-N(2)	121.11(7)	O(2)-C(29)-C(30)	109.0(3)
O(5)-K(1)-N(2)	118.47(8)	O(2)-C(29)-H(29A)	109.9
O(4)-K(1)-N(1)	118.10(7)	C(30)-C(29)-H(29A)	109.9
O(1)-K(1)-N(1)	60.58(8)	O(2)-C(29)-H(29B)	109.9
O(6)-K(1)-N(1)	120.27(8)	C(30)-C(29)-H(29B)	109.9
O(2)-K(1)-N(1)	120.20(8)	H(29A)-C(29)-H(29B)	108.3
O(3)-K(1)-N(1)	58.65(6)	N(2)-C(30)-C(29)	114.7(3)
O(5)-K(1)-N(1)	60.90(7)	N(2)-C(30)-H(30A)	108.6
N(2)-K(1)-N(1)	179.17(9)	C(29)-C(30)-H(30A)	108.6
C(31)-N(1)-C(37)	110.3(3)	N(2)-C(30)-H(30B)	108.6
C(31)-N(1)-C(25)	109.5(3)	C(29)-C(30)-H(30B)	108.6
C(37)-N(1)-C(25)	111.2(3)	H(30A)-C(30)-H(30B)	107.6
C(31)-N(1)-K(1)	111.27(18)	N(1)-C(31)-C(32)	112.6(3)
C(37)-N(1)-K(1)	106.24(18)	N(1)-C(31)-H(31A)	109.1
C(25)-N(1)-K(1)	108.4(2)	C(32)-C(31)-H(31A)	109.1
C(42)-N(2)-C(36)	109.0(3)	N(1)-C(31)-H(31B)	109.1
C(42)-N(2)-C(30)	110.4(3)	C(32)-C(31)-H(31B)	109.1
C(36)-N(2)-C(30)	110.9(3)	H(31A)-C(31)-H(31B)	107.8
C(42)-N(2)-K(1)	111.8(2)	O(3)-C(32)-C(31)	108.7(2)
C(36)-N(2)-K(1)	106.7(2)	O(3)-C(32)-H(32A)	110.0
C(30)-N(2)-K(1)	108.0(2)	C(31)-C(32)-H(32A)	110.0
C(26)-O(1)-C(27)	111.9(3)	O(3)-C(32)-H(32B)	110.0
C(26)-O(1)-K(1)	115.7(2)	C(31)-C(32)-H(32B)	110.0
C(27)-O(1)-K(1)	116.6(2)	H(32A)-C(32)-H(32B)	108.3
C(29)-O(2)-C(28)	111.7(3)	O(3)-C(33)-C(34)	108.9(2)
C(29)-O(2)-K(1)	116.7(2)	O(3)-C(33)-H(33A)	109.9
C(28)-O(2)-K(1)	113.19(19)	C(34)-C(33)-H(33A)	109.9
C(32)-O(3)-C(33)	111.7(2)	O(3)-C(33)-H(33B)	109.9
C(32)-O(3)-K(1)	116.67(16)	C(34)-C(33)-H(33B)	109.9
C(33)-O(3)-K(1)	114.19(17)	H(33A)-C(33)-H(33B)	108.3
C(34)-O(4)-C(35)	110.8(3)	O(4)-C(34)-C(33)	109.2(3)
C(34)-O(4)-K(1)	115.87(17)	O(4)-C(34)-H(34A)	109.8
C(35)-O(4)-K(1)	114.03(19)	C(33)-C(34)-H(34A)	109.8
C(38)-O(5)-C(39)	111.7(3)	O(4)-C(34)-H(34B)	109.8
C(38)-O(5)-K(1)	114.84(19)	C(33)-C(34)-H(34B)	109.8
C(39)-O(5)-K(1)	107.98(17)	H(34A)-C(34)-H(34B)	108.3
C(40)-O(6)-C(41)	112.5(3)	O(4)-C(35)-C(36)	108.3(4)
C(40)-O(6)-K(1)	118.24(19)	O(4)-C(35)-H(35A)	110.0
C(41)-O(6)-K(1)	115.73(18)	C(36)-C(35)-H(35A)	110.0
N(1)-C(25)-C(26)	113.9(3)	O(4)-C(35)-H(35B)	110.0
N(1)-C(25)-H(25A)	108.8	C(36)-C(35)-H(35B)	110.0
C(26)-C(25)-H(25A)	108.8	H(35A)-C(35)-H(35B)	108.4
N(1)-C(25)-H(25B)	108.8	N(2)-C(36)-C(35)	112.6(3)
C(26)-C(25)-H(25B)	108.8	N(2)-C(36)-H(36A)	109.1
H(25A)-C(25)-H(25B)	107.7	C(35)-C(36)-H(36A)	109.1
O(1)-C(26)-C(25)	108.9(3)	N(2)-C(36)-H(36B)	109.1
O(1)-C(26)-H(26A)	109.9	C(35)-C(36)-H(36B)	109.1
C(25)-C(26)-H(26A)	109.9	H(36A)-C(36)-H(36B)	107.8

N(1)-C(37)-C(38)	113.3(3)
N(1)-C(37)-H(37A)	108.9
C(38)-C(37)-H(37A)	108.9
N(1)-C(37)-H(37B)	108.9
C(38)-C(37)-H(37B)	108.9
H(37A)-C(37)-H(37B)	107.7
O(5)-C(38)-C(37)	109.7(3)
O(5)-C(38)-H(38A)	109.7
C(37)-C(38)-H(38A)	109.7
O(5)-C(38)-H(38B)	109.7
C(37)-C(38)-H(38B)	109.7
H(38A)-C(38)-H(38B)	108.2
O(5)-C(39)-C(40)	109.3(2)
O(5)-C(39)-H(39A)	109.8
C(40)-C(39)-H(39A)	109.8
O(5)-C(39)-H(39B)	109.8
C(40)-C(39)-H(39B)	109.8
H(39A)-C(39)-H(39B)	108.3
O(6)-C(40)-C(39)	109.1(3)
O(6)-C(40)-H(40A)	109.9
C(39)-C(40)-H(40A)	109.9
O(6)-C(40)-H(40B)	109.9
C(39)-C(40)-H(40B)	109.9
H(40A)-C(40)-H(40B)	108.3
O(6)-C(41)-C(42)	108.3(3)
O(6)-C(41)-H(41A)	110.0
C(42)-C(41)-H(41A)	110.0
O(6)-C(41)-H(41B)	110.0
C(42)-C(41)-H(41B)	110.0
H(41A)-C(41)-H(41B)	108.4
N(2)-C(42)-C(41)	112.9(3)
N(2)-C(42)-H(42A)	109.0
C(41)-C(42)-H(42A)	109.0
N(2)-C(42)-H(42B)	109.0
C(41)-C(42)-H(42B)	109.0
H(42A)-C(42)-H(42B)	107.8

Symmetry transformations used to generate equivalent atoms:

Table S-4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3**.
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}
Ge(1)	25(1)	30(1)	28(1)	-5(1)	1(1)	-10(1)
Si(1)	35(1)	35(1)	28(1)	-6(1)	-4(1)	-3(1)
Si(2)	28(1)	51(1)	33(1)	-12(1)	2(1)	-17(1)
Si(3)	39(1)	30(1)	32(1)	-4(1)	2(1)	-10(1)
F(1)	65(1)	59(1)	47(1)	-25(1)	-14(1)	-7(1)
F(2)	37(1)	100(2)	58(1)	-4(1)	-11(1)	-31(1)
F(3)	67(1)	32(1)	47(1)	-1(1)	2(1)	-7(1)
C(1)	23(1)	27(1)	32(1)	0(1)	-3(1)	-7(1)
C(2)	27(1)	26(1)	36(1)	-3(1)	-7(1)	-5(1)
C(3)	38(2)	40(2)	56(2)	-11(1)	-13(1)	-14(1)
C(4)	34(2)	45(2)	78(2)	-6(2)	-10(1)	-21(1)
C(5)	25(1)	45(2)	63(2)	1(1)	5(1)	-12(1)
C(6)	28(1)	34(1)	41(2)	-2(1)	2(1)	-9(1)
C(7)	59(2)	46(2)	34(2)	0(1)	11(1)	-2(1)
C(8)	34(1)	42(2)	42(2)	-8(1)	1(1)	-2(1)
C(9)	28(1)	34(1)	28(1)	-9(1)	2(1)	-8(1)
C(10)	31(1)	42(1)	28(1)	-9(1)	0(1)	-11(1)
C(11)	43(2)	62(2)	36(2)	-6(1)	-13(1)	-16(1)
C(12)	59(2)	51(2)	33(2)	4(1)	-13(1)	-12(2)
C(13)	53(2)	38(2)	34(1)	-1(1)	2(1)	-14(1)
C(14)	37(1)	34(1)	39(1)	-4(1)	-2(1)	-13(1)
C(15)	37(2)	50(2)	53(2)	-23(1)	16(1)	-20(1)
C(16)	41(2)	57(2)	57(2)	-29(2)	13(1)	-25(1)
C(17)	29(1)	34(1)	29(1)	-7(1)	1(1)	-12(1)
C(18)	32(1)	31(1)	34(1)	-9(1)	2(1)	-12(1)
C(19)	49(2)	34(1)	48(2)	-13(1)	4(1)	-12(1)
C(20)	67(2)	50(2)	49(2)	-27(2)	11(2)	-17(2)
C(21)	68(2)	55(2)	33(2)	-16(1)	10(1)	-18(2)
C(22)	50(2)	42(2)	32(1)	-9(1)	6(1)	-14(1)
C(23)	48(2)	43(2)	41(2)	-7(1)	8(1)	-21(1)
C(24)	40(2)	44(2)	34(1)	-3(1)	-4(1)	-10(1)
K(1)	34(1)	31(1)	41(1)	-9(1)	-1(1)	-9(1)
N(1)	67(2)	49(2)	43(1)	-19(1)	-15(1)	11(1)
N(2)	79(2)	41(1)	41(1)	2(1)	6(1)	2(1)
O(1)	45(1)	52(1)	85(2)	-28(1)	-26(1)	2(1)
O(2)	43(1)	47(1)	80(2)	-20(1)	16(1)	-20(1)
O(3)	42(1)	27(1)	58(1)	-10(1)	-3(1)	-9(1)
O(4)	56(1)	35(1)	68(2)	-3(1)	18(1)	-3(1)
O(5)	44(1)	43(1)	52(1)	-5(1)	14(1)	-8(1)
O(6)	62(1)	41(1)	60(1)	-8(1)	-17(1)	-21(1)
C(25)	84(3)	95(3)	70(3)	-47(2)	-41(2)	23(2)
C(26)	75(3)	96(3)	87(3)	-43(3)	-47(2)	23(2)
C(27)	35(2)	50(2)	134(4)	-33(2)	-21(2)	-5(2)
C(28)	39(2)	54(2)	138(4)	-30(2)	12(2)	-20(2)
C(29)	73(3)	71(3)	83(3)	-25(2)	49(2)	-22(2)
C(30)	89(3)	51(2)	53(2)	-13(2)	22(2)	-2(2)
C(31)	70(2)	56(2)	53(2)	-32(2)	-8(2)	4(2)
C(32)	54(2)	47(2)	80(2)	-36(2)	-12(2)	-5(2)
C(33)	56(2)	28(1)	84(3)	-5(2)	21(2)	-11(1)
C(34)	64(2)	39(2)	60(2)	11(2)	18(2)	9(2)
C(35)	132(4)	65(2)	48(2)	16(2)	10(2)	34(3)
C(36)	141(4)	53(2)	57(2)	17(2)	33(2)	19(2)
C(37)	129(4)	57(2)	29(2)	-6(2)	11(2)	10(2)
C(38)	91(3)	48(2)	76(3)	-14(2)	51(2)	-16(2)
C(39)	33(2)	49(2)	108(3)	10(2)	1(2)	-17(1)
C(40)	55(2)	45(2)	98(3)	-7(2)	-27(2)	-23(2)
C(41)	80(2)	64(2)	57(2)	-29(2)	-28(2)	-14(2)
C(42)	97(3)	76(3)	45(2)	-11(2)	-30(2)	4(2)

Table S-5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **3**.

	x	y	z	U(eq)
H(3A)	-1307	863	6546	51
H(4A)	-3035	1080	7424	61
H(5A)	-3316	2073	8455	55
H(6A)	-1850	2853	8592	43
H(7A)	1589	2437	5095	78
H(7B)	1571	2981	5865	78
H(7C)	332	3165	5441	78
H(8A)	2083	-13	7135	63
H(8B)	2462	994	7210	63
H(8C)	2920	451	6415	63
H(11A)	3789	1384	9885	56
H(12A)	2837	236	10709	59
H(13A)	1006	143	10327	52
H(14A)	129	1218	9142	44
H(15A)	4601	2960	7159	67
H(15B)	3353	2776	7008	67
H(15C)	4420	1820	7448	67
H(16A)	1757	4507	8205	71
H(16B)	3031	4740	7937	71
H(16C)	2602	4524	8894	71
H(19A)	-1557	6766	7991	52
H(20A)	-1934	6478	9413	65
H(21A)	-1377	4770	10159	62
H(22A)	-417	3370	9496	50
H(23A)	1099	5678	5713	65
H(23B)	1567	4650	6400	65
H(23C)	1476	5781	6581	65
H(24A)	-2208	5294	6286	61
H(24B)	-1111	4218	6380	61
H(24C)	-1119	5122	5588	61
H(25A)	3206	6714	5167	104
H(25B)	3309	7649	4427	104
H(26A)	2211	8882	5291	108
H(26B)	1420	8185	5107	108
H(27A)	192	8128	6295	85
H(27B)	657	9040	6489	85
H(28A)	-123	8141	7689	90
H(28B)	914	7075	7554	90
H(29A)	1606	7067	8904	94
H(29B)	550	8158	8934	94
H(30A)	2049	8986	8940	84
H(30B)	2042	8102	9741	84
H(31A)	6178	6587	5228	74
H(31B)	5319	6331	4667	74
H(32A)	4494	5449	5875	70
H(32B)	5928	4906	5716	70
H(33A)	6368	4213	7062	71
H(33B)	4936	4567	7318	71
H(34A)	6135	4354	8445	78
H(34B)	6658	5277	7940	78
H(35A)	5725	6350	9012	123
H(35B)	5416	5297	9476	123
H(36A)	3279	6290	9416	123
H(36B)	3998	6638	10016	123
H(37A)	4043	8996	4919	99
H(37B)	5067	8293	4364	99
H(38A)	6422	7878	5472	93
H(38B)	6071	9080	5007	93
H(39A)	6645	9388	6230	80

H(39B)	6743	8240	6762	80
H(40A)	6205	9569	7597	75
H(40B)	4959	10103	7133	75
H(41A)	3591	9657	8388	77
H(41B)	4855	9575	8741	77
H(42A)	5078	7818	9343	93
H(42B)	3866	8589	9703	93

Table S-6. Torsion angles [°] for **3**.

C(9)-Ge(1)-C(1)-C(6)	74.8(2)
C(17)-Ge(1)-C(1)-C(6)	-24.9(2)
C(9)-Ge(1)-C(1)-C(2)	-105.41(19)
C(17)-Ge(1)-C(1)-C(2)	154.88(19)
C(6)-C(1)-C(2)-C(3)	-1.2(3)
Ge(1)-C(1)-C(2)-C(3)	178.97(18)
C(6)-C(1)-C(2)-Si(1)	-178.99(17)
Ge(1)-C(1)-C(2)-Si(1)	1.2(3)
F(1)-Si(1)-C(2)-C(3)	3.8(2)
C(8)-Si(1)-C(2)-C(3)	-109.1(2)
C(7)-Si(1)-C(2)-C(3)	117.1(2)
F(1)-Si(1)-C(2)-C(1)	-178.44(19)
C(8)-Si(1)-C(2)-C(1)	68.7(2)
C(7)-Si(1)-C(2)-C(1)	-65.1(2)
C(1)-C(2)-C(3)-C(4)	0.9(4)
Si(1)-C(2)-C(3)-C(4)	178.8(2)
C(2)-C(3)-C(4)-C(5)	-0.3(4)
C(3)-C(4)-C(5)-C(6)	0.0(4)
C(4)-C(5)-C(6)-C(1)	-0.4(4)
C(2)-C(1)-C(6)-C(5)	1.0(4)
Ge(1)-C(1)-C(6)-C(5)	-179.2(2)
C(1)-Ge(1)-C(9)-C(14)	-12.1(2)
C(17)-Ge(1)-C(9)-C(14)	89.7(2)
C(1)-Ge(1)-C(9)-C(10)	167.90(19)
C(17)-Ge(1)-C(9)-C(10)	-90.3(2)
C(14)-C(9)-C(10)-C(11)	-1.2(4)
Ge(1)-C(9)-C(10)-C(11)	178.8(2)
C(14)-C(9)-C(10)-Si(2)	177.75(18)
Ge(1)-C(9)-C(10)-Si(2)	-2.2(3)
F(2)-Si(2)-C(10)-C(11)	-2.7(2)
C(16)-Si(2)-C(10)-C(11)	-115.7(2)
C(15)-Si(2)-C(10)-C(11)	111.0(2)
F(2)-Si(2)-C(10)-C(9)	178.2(2)
C(16)-Si(2)-C(10)-C(9)	65.3(2)
C(15)-Si(2)-C(10)-C(9)	-68.0(2)
C(9)-C(10)-C(11)-C(12)	-0.2(4)
Si(2)-C(10)-C(11)-C(12)	-179.3(2)
C(10)-C(11)-C(12)-C(13)	1.2(5)
C(11)-C(12)-C(13)-C(14)	-0.7(4)
C(12)-C(13)-C(14)-C(9)	-0.8(4)
C(10)-C(9)-C(14)-C(13)	1.8(4)
Ge(1)-C(9)-C(14)-C(13)	-178.2(2)
C(1)-Ge(1)-C(17)-C(22)	83.3(2)
C(9)-Ge(1)-C(17)-C(22)	-17.6(2)
C(1)-Ge(1)-C(17)-C(18)	-103.4(2)
C(9)-Ge(1)-C(17)-C(18)	155.74(19)
C(22)-C(17)-C(18)-C(19)	0.6(4)
Ge(1)-C(17)-C(18)-C(19)	-173.04(19)
C(22)-C(17)-C(18)-Si(3)	-178.52(19)
Ge(1)-C(17)-C(18)-Si(3)	7.8(3)
F(3)-Si(3)-C(18)-C(19)	-3.6(2)
C(24)-Si(3)-C(18)-C(19)	-116.1(2)
C(23)-Si(3)-C(18)-C(19)	110.2(2)
F(3)-Si(3)-C(18)-C(17)	175.6(2)
C(24)-Si(3)-C(18)-C(17)	63.1(2)
C(23)-Si(3)-C(18)-C(17)	-70.7(2)
C(17)-C(18)-C(19)-C(20)	0.1(4)
Si(3)-C(18)-C(19)-C(20)	179.3(2)
C(18)-C(19)-C(20)-C(21)	-0.8(5)
C(19)-C(20)-C(21)-C(22)	0.7(5)
C(20)-C(21)-C(22)-C(17)	0.0(5)
C(18)-C(17)-C(22)-C(21)	-0.7(4)
Ge(1)-C(17)-C(22)-C(21)	172.9(2)
O(4)-K(1)-N(1)-C(31)	-14.7(3)
O(1)-K(1)-N(1)-C(31)	-127.4(2)
O(6)-K(1)-N(1)-C(31)	96.4(2)
O(2)-K(1)-N(1)-C(31)	-134.0(2)
O(3)-K(1)-N(1)-C(31)	-8.5(2)
O(5)-K(1)-N(1)-C(31)	104.6(2)
N(2)-K(1)-N(1)-C(31)	65(5)
O(4)-K(1)-N(1)-C(37)	-134.8(2)
O(1)-K(1)-N(1)-C(37)	112.5(2)
O(6)-K(1)-N(1)-C(37)	-23.7(2)
O(2)-K(1)-N(1)-C(37)	105.9(2)
O(3)-K(1)-N(1)-C(37)	-128.6(2)
O(5)-K(1)-N(1)-C(37)	-15.5(2)
N(2)-K(1)-N(1)-C(37)	-55(5)
O(4)-K(1)-N(1)-C(25)	105.6(2)
O(1)-K(1)-N(1)-C(25)	-7.0(2)
O(6)-K(1)-N(1)-C(25)	-143.2(2)
O(2)-K(1)-N(1)-C(25)	-13.6(2)
O(3)-K(1)-N(1)-C(25)	111.9(2)
O(5)-K(1)-N(1)-C(25)	-135.0(2)
N(2)-K(1)-N(1)-C(25)	-175(61)
O(4)-K(1)-N(2)-C(42)	108.2(2)
O(1)-K(1)-N(2)-C(42)	-139.5(2)
O(6)-K(1)-N(2)-C(42)	-3.7(2)
O(2)-K(1)-N(2)-C(42)	-133.1(2)
O(3)-K(1)-N(2)-C(42)	101.0(2)
O(5)-K(1)-N(2)-C(42)	-11.3(2)
N(1)-K(1)-N(2)-C(42)	28(5)
O(4)-K(1)-N(2)-C(36)	-10.9(3)
O(1)-K(1)-N(2)-C(36)	101.4(3)
O(6)-K(1)-N(2)-C(36)	-122.7(3)
O(2)-K(1)-N(2)-C(36)	107.8(3)
O(3)-K(1)-N(2)-C(36)	-18.1(3)
O(5)-K(1)-N(2)-C(36)	-130.4(3)
N(1)-K(1)-N(2)-C(36)	-91(5)
O(4)-K(1)-N(2)-C(30)	-130.2(2)
O(1)-K(1)-N(2)-C(30)	-17.9(2)
O(6)-K(1)-N(2)-C(30)	118.0(2)
O(2)-K(1)-N(2)-C(30)	-11.5(2)
O(3)-K(1)-N(2)-C(30)	-137.4(2)
O(5)-K(1)-N(2)-C(30)	110.3(2)
N(1)-K(1)-N(2)-C(30)	150(5)
O(4)-K(1)-O(1)-C(26)	-132.9(2)
O(6)-K(1)-O(1)-C(26)	76.3(2)
O(2)-K(1)-O(1)-C(26)	147.1(2)
O(3)-K(1)-O(1)-C(26)	-75.0(2)
O(5)-K(1)-O(1)-C(26)	18.8(2)
N(2)-K(1)-O(1)-C(26)	153.6(2)
N(1)-K(1)-O(1)-C(26)	-26.2(2)
O(4)-K(1)-O(1)-C(27)	92.3(2)
O(6)-K(1)-O(1)-C(27)	-58.5(3)
O(2)-K(1)-O(1)-C(27)	12.3(2)
O(3)-K(1)-O(1)-C(27)	150.2(2)
O(5)-K(1)-O(1)-C(27)	-116.0(2)
N(2)-K(1)-O(1)-C(27)	18.8(3)
N(1)-K(1)-O(1)-C(27)	-161.0(3)
O(4)-K(1)-O(2)-C(29)	30.3(2)
O(1)-K(1)-O(2)-C(29)	152.7(2)
O(6)-K(1)-O(2)-C(29)	-63.7(2)
O(3)-K(1)-O(2)-C(29)	85.4(2)
O(5)-K(1)-O(2)-C(29)	-125.1(2)

N(2)-K(1)-O(2)-C(29)	-21.0(2)
N(1)-K(1)-O(2)-C(29)	159.4(2)
O(4)-K(1)-O(2)-C(28)	-101.5(2)
O(1)-K(1)-O(2)-C(28)	20.9(2)
O(6)-K(1)-O(2)-C(28)	164.5(2)
O(3)-K(1)-O(2)-C(28)	-46.4(2)
O(5)-K(1)-O(2)-C(28)	103.2(2)
N(2)-K(1)-O(2)-C(28)	-152.7(2)
N(1)-K(1)-O(2)-C(28)	27.6(2)
O(4)-K(1)-O(3)-C(32)	148.6(2)
O(1)-K(1)-O(3)-C(32)	25.1(2)
O(6)-K(1)-O(3)-C(32)	-135.7(2)
O(2)-K(1)-O(3)-C(32)	78.5(2)
O(5)-K(1)-O(3)-C(32)	-78.5(2)
N(2)-K(1)-O(3)-C(32)	155.9(2)
N(1)-K(1)-O(3)-C(32)	-25.0(2)
O(4)-K(1)-O(3)-C(33)	15.8(2)
O(1)-K(1)-O(3)-C(33)	-107.7(2)
O(6)-K(1)-O(3)-C(33)	91.5(2)
O(2)-K(1)-O(3)-C(33)	-54.3(2)
O(5)-K(1)-O(3)-C(33)	148.7(2)
N(2)-K(1)-O(3)-C(33)	23.1(2)
N(1)-K(1)-O(3)-C(33)	-157.8(2)
O(1)-K(1)-O(4)-C(34)	95.9(2)
O(6)-K(1)-O(4)-C(34)	-101.5(2)
O(2)-K(1)-O(4)-C(34)	155.2(2)
O(3)-K(1)-O(4)-C(34)	18.6(2)
O(5)-K(1)-O(4)-C(34)	-48.6(3)
N(2)-K(1)-O(4)-C(34)	-154.3(3)
N(1)-K(1)-O(4)-C(34)	24.8(3)
O(1)-K(1)-O(4)-C(35)	-133.8(3)
O(6)-K(1)-O(4)-C(35)	28.9(3)
O(2)-K(1)-O(4)-C(35)	-74.4(3)
O(3)-K(1)-O(4)-C(35)	149.0(3)
O(5)-K(1)-O(4)-C(35)	81.8(3)
N(2)-K(1)-O(4)-C(35)	-23.9(3)
N(1)-K(1)-O(4)-C(35)	155.2(3)
O(4)-K(1)-O(5)-C(38)	86.2(3)
O(1)-K(1)-O(5)-C(38)	-63.3(3)
O(6)-K(1)-O(5)-C(38)	153.3(3)
O(2)-K(1)-O(5)-C(38)	-125.2(2)
O(3)-K(1)-O(5)-C(38)	33.3(3)
N(2)-K(1)-O(5)-C(38)	160.9(2)
N(1)-K(1)-O(5)-C(38)	-18.5(2)
O(4)-K(1)-O(5)-C(39)	-39.2(2)
O(1)-K(1)-O(5)-C(39)	171.26(18)
O(6)-K(1)-O(5)-C(39)	27.92(18)
O(2)-K(1)-O(5)-C(39)	109.45(19)
O(3)-K(1)-O(5)-C(39)	-92.06(19)
N(2)-K(1)-O(5)-C(39)	35.5(2)
N(1)-K(1)-O(5)-C(39)	-143.9(2)
O(4)-K(1)-O(6)-C(40)	138.4(2)
O(1)-K(1)-O(6)-C(40)	-66.1(3)
O(2)-K(1)-O(6)-C(40)	-123.1(2)
O(3)-K(1)-O(6)-C(40)	81.5(2)
O(5)-K(1)-O(6)-C(40)	5.5(2)
N(2)-K(1)-O(6)-C(40)	-166.7(2)
N(1)-K(1)-O(6)-C(40)	13.8(2)
O(4)-K(1)-O(6)-C(41)	-83.8(2)
O(1)-K(1)-O(6)-C(41)	71.7(2)
O(2)-K(1)-O(6)-C(41)	14.7(2)
O(3)-K(1)-O(6)-C(41)	-140.73(19)
O(5)-K(1)-O(6)-C(41)	143.3(2)
N(2)-K(1)-O(6)-C(41)	-28.9(2)
N(1)-K(1)-O(6)-C(41)	151.58(19)
C(31)-N(1)-C(25)-C(26)	159.9(4)
C(37)-N(1)-C(25)-C(26)	-78.0(4)
K(1)-N(1)-C(25)-C(26)	38.4(4)
C(27)-O(1)-C(26)-C(25)	-165.7(3)
K(1)-O(1)-C(26)-C(25)	57.5(4)
N(1)-C(25)-C(26)-O(1)	-65.6(5)
C(26)-O(1)-C(27)-C(28)	179.9(3)
K(1)-O(1)-C(27)-C(28)	-43.6(3)
C(29)-O(2)-C(28)-C(27)	173.6(3)
K(1)-O(2)-C(28)-C(27)	-52.2(3)
O(1)-C(27)-C(28)-O(2)	63.9(3)
C(28)-O(2)-C(29)-C(30)	-175.9(3)
K(1)-O(2)-C(29)-C(30)	51.7(3)
C(42)-N(2)-C(30)-C(29)	166.1(3)
C(36)-N(2)-C(30)-C(29)	-73.0(4)
K(1)-N(2)-C(30)-C(29)	43.6(3)
O(2)-C(29)-C(30)-N(2)	-65.8(4)
C(37)-N(1)-C(31)-C(32)	157.6(3)
C(25)-N(1)-C(31)-C(32)	-79.8(4)
K(1)-N(1)-C(31)-C(32)	40.0(3)
C(33)-O(3)-C(32)-C(31)	-169.6(3)
K(1)-O(3)-C(32)-C(31)	56.5(3)
N(1)-C(31)-C(32)-O(3)	-64.8(4)
C(32)-O(3)-C(33)-C(34)	178.0(3)
K(1)-O(3)-C(33)-C(34)	-46.9(3)
C(35)-O(4)-C(34)-C(33)	177.7(3)
K(1)-O(4)-C(34)-C(33)	-50.4(3)
O(3)-C(33)-C(34)-O(4)	64.8(3)
C(34)-O(4)-C(35)-C(36)	-170.0(3)
K(1)-O(4)-C(35)-C(36)	57.2(4)
C(42)-N(2)-C(36)-C(35)	-76.5(5)
C(30)-N(2)-C(36)-C(35)	161.7(4)
K(1)-N(2)-C(36)-C(35)	44.3(5)
O(4)-C(35)-C(36)-N(2)	-71.0(5)
C(31)-N(1)-C(37)-C(38)	-71.9(3)
C(25)-N(1)-C(37)-C(38)	166.5(3)
K(1)-N(1)-C(37)-C(38)	48.8(3)
C(39)-O(5)-C(38)-C(37)	174.6(3)
K(1)-O(5)-C(38)-C(37)	51.1(3)
N(1)-C(37)-C(38)-O(5)	-71.1(4)
C(38)-O(5)-C(39)-C(40)	172.8(3)
K(1)-O(5)-C(39)-C(40)	-60.0(3)
C(41)-O(6)-C(40)-C(39)	-176.2(3)
K(1)-O(6)-C(40)-C(39)	-37.1(3)
O(5)-C(39)-C(40)-O(6)	66.7(3)
C(40)-O(6)-C(41)-C(42)	-159.8(3)
K(1)-O(6)-C(41)-C(42)	60.1(3)
C(36)-N(2)-C(42)-C(41)	152.5(3)
C(30)-N(2)-C(42)-C(41)	-85.4(4)
K(1)-N(2)-C(42)-C(41)	34.9(4)
O(6)-C(41)-C(42)-N(2)	-62.9(4)

Symmetry transformations used to generate equivalent atoms:

3. Computational Details.

All calculations were performed with the Gaussian 98 program package the on HIT HPC-PA264U-6CPU model: Gaussian 98, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Oritz, J. V. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, M. W. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

Table S-7. xyz Coordinates of the optimized structure of **3** without a pottasium and a cryptand at B3LYP/6-31G(d) level.

Ge	-0.023749	-0.034169	-0.070099
C	-0.307885	-0.810514	1.815646
C	1.978704	0.419356	0.074393
C	-0.799817	1.847361	0.243634
C	-0.245879	-2.214385	2.047372
C	-0.629359	0.013609	2.910113
C	2.758430	0.664166	-1.091833
C	2.643262	0.442492	1.315235
C	-2.157656	2.141250	-0.069262
C	0.000823	2.907031	0.710995
Si	0.129172	-3.500919	0.720382
Si	2.083809	0.642698	-2.852144
Si	-3.390092	0.892154	-0.757192
C	-0.485463	-2.718179	3.342319
C	-0.875611	-0.500395	4.186749
H	-0.687779	1.089102	2.761019
C	4.135991	0.936698	-0.963147
C	4.010988	0.703565	1.426803
H	2.073391	0.253561	2.221626
C	-2.648658	3.449300	0.116840
C	-0.495837	4.202080	0.881064
H	1.043646	2.714954	0.951736
F	0.137936	-4.931399	1.542398
F	3.380265	1.062592	-3.781082
F	-4.799402	1.740609	-0.871371
H	-0.428128	-3.788918	3.516135
C	-0.800834	-1.873985	4.407752
H	-1.121325	0.175915	5.005756
C	-1.218539	-3.720540	-0.575443
C	1.848563	-3.389508	-0.032708
H	4.725430	1.133156	-1.855848

C	4.765036	0.955937	0.281658
H	4.484159	0.711304	2.408633
C	1.591545	-1.057266	-3.496245
C	0.796144	1.962521	-3.223443
H	-3.688314	3.666398	-0.115307
C	-1.830587	4.477630	0.585935
H	0.159824	4.991249	1.245789
C	-3.042190	0.327423	-2.519394
C	-3.801423	-0.538862	0.392197
H	-0.988267	-2.287734	5.397133
H	-0.982929	-4.562678	-1.239320
H	-1.321217	-2.813685	-1.178422
H	-2.182626	-3.926157	-0.094548
H	2.607657	-3.467212	0.755031
H	2.006039	-2.438829	-0.550056
H	2.013206	-4.206594	-0.747189
H	5.831879	1.163061	0.354069
H	1.306252	-1.001896	-4.554810
H	0.747671	-1.456936	-2.925354
H	2.430666	-1.758170	-3.406142
H	-0.095887	1.845322	-2.601389
H	0.492621	1.925162	-4.278164
H	1.211935	2.957097	-3.022122
H	-2.231324	5.481633	0.716150
H	-3.852859	-0.313742	-2.889126
H	-2.102471	-0.231479	-2.562037
H	-2.958504	1.191725	-3.190425
H	-4.194005	-0.155742	1.341344
H	-2.918383	-1.142489	0.621776
H	-4.564149	-1.189066	-0.055923

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