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Fluorinated triazapentadienyl ligand supported ethyl zinc(II) complexes: reaction with dioxygen and catalytic applications in the Tishchenko reaction

Naveen V. Kulkarni, Animesh Das, Shawn G. Ridlen, Erin Maxfield, Venkata A. K. Adiraju, Muhammed Yousufuddin, H. V. Rasika Dias*

Supporting Information

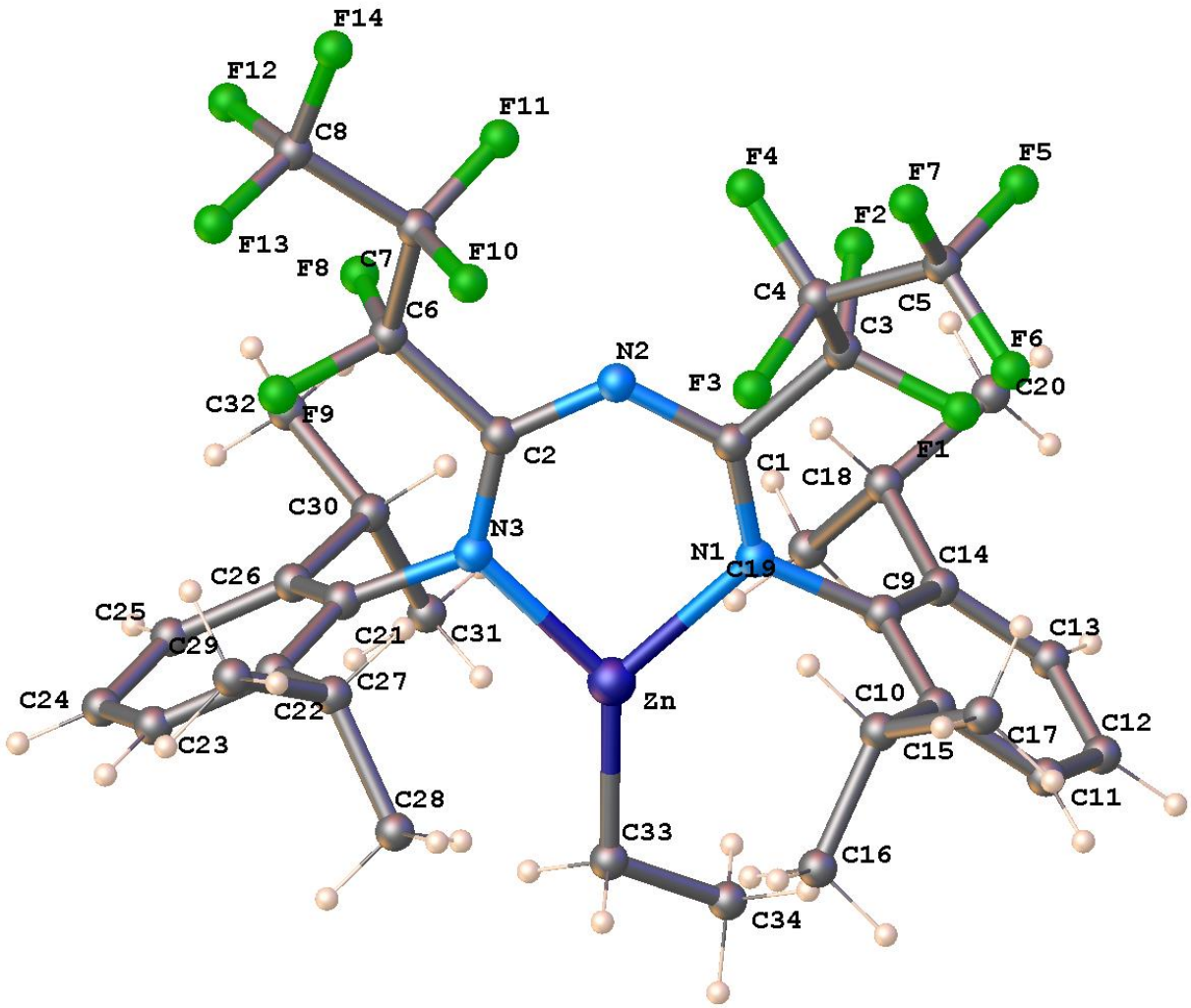


Table S1. Crystal data and structure refinement for $[N\{(C_3F_7)C(Dipp)N\}_2]ZnEt$ (**1**).

Identification code	rad2_0m
Empirical formula	$C_{34}H_{39}F_{14}N_3Zn$
Formula weight	821.05
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	10.2646(6)
b/Å	12.3503(7)
c/Å	15.2654(8)
α/°	71.6280(10)
β/°	86.7850(10)
γ/°	87.1630(10)
Volume/Å^3	1832.65(18)

Z	2
ρ_{calc}g/cm^3	1.488
μ/mm^{-1}	0.770
F(000)	840.0
Crystal size/mm^3	0.15 × 0.1 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.63 to 52.998
Index ranges	$-12 \leq h \leq 12$, $-15 \leq k \leq 15$, $-19 \leq l \leq 19$
Reflections collected	20859
Independent reflections	7560 [R_{int} = 0.0175, R_{sigma} = 0.0207]
Data/restraints/parameters	7560/0/478
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0297, wR_2 = 0.0715
Final R indexes [all data]	R_1 = 0.0345, wR_2 = 0.0740
Largest diff. peak/hole / e Å^{-3}	0.66/-0.39

Table S2. Bond Lengths for [N{(C_3F_7)C(Dipp)N}$_2$]ZnEt (**1**).

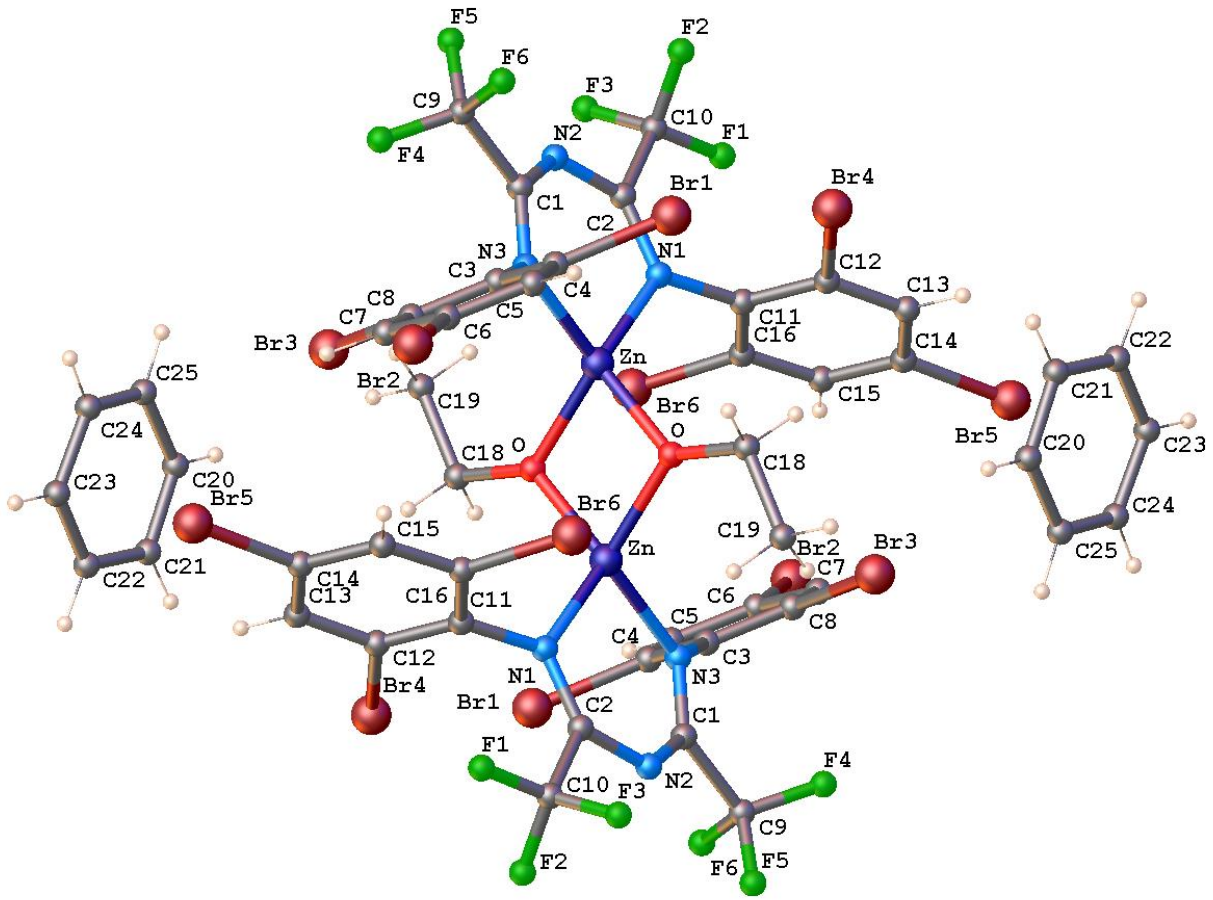
Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zn	N1	1.9931(13)	C6	C7	1.540(2)
Zn	N3	1.9855(13)	C7	C8	1.552(2)
Zn	C33	1.9515(16)	C9	C10	1.402(2)
F1	C3	1.3521(17)	C9	C14	1.401(2)
F2	C3	1.3500(18)	C10	C11	1.394(2)
F3	C4	1.3430(18)	C10	C15	1.519(2)
F4	C4	1.3358(18)	C11	C12	1.383(2)
F5	C5	1.3280(19)	C12	C13	1.381(2)
F6	C5	1.323(2)	C13	C14	1.392(2)
F7	C5	1.3283(19)	C14	C18	1.519(2)
F8	C6	1.348(2)	C15	C16	1.526(2)
F9	C6	1.344(2)	C15	C17	1.533(2)
F10	C7	1.334(2)	C18	C19	1.520(3)
F11	C7	1.340(2)	C18	C20	1.526(3)
F12	C8	1.319(2)	C21	C22	1.404(2)
F13	C8	1.315(2)	C21	C26	1.402(2)
F14	C8	1.334(2)	C22	C23	1.391(2)
N1	C1	1.301(2)	C22	C27	1.518(2)
N1	C9	1.4518(18)	C23	C24	1.381(3)

N2	C1	1.340(2)	C24	C25	1.379(3)
N2	C2	1.334(2)	C25	C26	1.396(2)
N3	C2	1.306(2)	C26	C30	1.523(2)
N3	C21	1.4499(19)	C27	C28	1.528(3)
C1	C3	1.541(2)	C27	C29	1.525(3)
C2	C6	1.551(2)	C30	C31	1.534(2)
C3	C4	1.554(2)	C30	C32	1.528(2)
C4	C5	1.545(2)	C33	C34	1.531(2)

Table S3 Bond Angles for [N{(C_3F_7)C(Dipp)N}$_2$]ZnEt (**1**).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N3	Zn	N1	92.37(5)	C6	C7	C8	114.47(14)
C33	Zn	N1	133.69(6)	F12	C8	F14	107.72(17)
C33	Zn	N3	133.94(6)	F12	C8	C7	111.24(16)
C1	N1	Zn	122.59(10)	F13	C8	F12	108.81(16)
C1	N1	C9	126.60(13)	F13	C8	F14	108.61(17)
C9	N1	Zn	110.80(9)	F13	C8	C7	112.19(16)
C2	N2	C1	124.99(13)	F14	C8	C7	108.14(15)
C2	N3	Zn	122.90(10)	C10	C9	N1	118.52(13)
C2	N3	C21	124.36(13)	C14	C9	N1	118.74(13)
C21	N3	Zn	112.60(9)	C14	C9	C10	122.16(14)
N1	C1	N2	128.59(14)	C9	C10	C15	122.44(14)
N1	C1	C3	122.96(13)	C11	C10	C9	117.86(14)
N2	C1	C3	108.46(13)	C11	C10	C15	119.70(14)
N2	C2	C6	110.69(13)	C12	C11	C10	121.00(15)
N3	C2	N2	128.42(14)	C13	C12	C11	119.89(15)
N3	C2	C6	120.86(13)	C12	C13	C14	121.60(15)
F1	C3	C1	112.16(12)	C9	C14	C18	122.31(14)
F1	C3	C4	106.67(12)	C13	C14	C9	117.43(14)
F2	C3	F1	106.68(12)	C13	C14	C18	120.26(14)
F2	C3	C1	110.06(12)	C10	C15	C16	111.03(13)
F2	C3	C4	108.27(12)	C10	C15	C17	111.48(13)
C1	C3	C4	112.72(12)	C16	C15	C17	110.03(14)
F3	C4	C3	108.98(13)	C14	C18	C19	110.70(14)
F3	C4	C5	106.63(13)	C14	C18	C20	111.90(14)
F4	C4	F3	109.23(13)	C19	C18	C20	110.92(17)
F4	C4	C3	110.27(13)	C22	C21	N3	118.83(14)

F4	C4	C5	106.49(13)	C26	C21	N3	118.53(14)
C5	C4	C3	115.06(13)	C26	C21	C22	122.34(15)
F5	C5	F7	108.15(14)	C21	C22	C27	121.39(15)
F5	C5	C4	110.21(13)	C23	C22	C21	117.60(15)
F6	C5	F5	108.67(13)	C23	C22	C27	121.01(15)
F6	C5	F7	107.79(14)	C24	C23	C22	121.14(17)
F6	C5	C4	112.52(14)	C25	C24	C23	120.29(16)
F7	C5	C4	109.38(13)	C24	C25	C26	121.25(16)
F8	C6	C2	108.06(13)	C21	C26	C30	122.48(14)
F8	C6	C7	108.03(14)	C25	C26	C21	117.36(15)
F9	C6	F8	106.69(14)	C25	C26	C30	120.12(15)
F9	C6	C2	111.60(13)	C22	C27	C28	110.45(15)
F9	C6	C7	105.45(13)	C22	C27	C29	112.90(15)
C7	C6	C2	116.54(13)	C29	C27	C28	109.99(17)
F10	C7	F11	110.19(14)	C26	C30	C31	110.31(14)
F10	C7	C6	109.29(14)	C26	C30	C32	112.27(15)
F10	C7	C8	106.59(14)	C32	C30	C31	110.19(14)
F11	C7	C6	109.70(14)	C34	C33	Zn	115.93(12)
F11	C7	C8	106.51(14)				



Unit cell of $\{[N\{(CF_3)C(2,4,6\text{-}Br_3C_6H_2)N\}_2]ZnOEt\}_2 \bullet 2(C_6H_6)$

Table S4 Crystal data and structure refinement for $\{[N\{(CF_3)C(2,4,6\text{-}Br_3C_6H_2)N\}_2]ZnOEt\}_2 \bullet 2(C_6H_6)$.

Identification code	rad156_0m_a
Empirical formula	$C_{48}H_{30}Br_{12}F_{12}N_6O_2Zn_2$
Formula weight	2040.44
Temperature/K	100.01
Crystal system	triclinic
Space group	P-1
a/Å	11.462(2)
b/Å	11.6254(19)
c/Å	14.089(2)
α/°	67.401(3)

β/°	89.479(4)
γ/°	63.532(3)
Volume/Å^3	1521.4(4)
Z	1
ρ_{calc}g/cm^3	2.227
μ/mm^{-1}	8.748
F(000)	964.0
Crystal size/mm^3	0.538 × 0.296 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.004 to 53.464
Index ranges	$-14 \leq h \leq 14$, $-14 \leq k \leq 14$, $-17 \leq l \leq 17$
Reflections collected	13064
Independent reflections	6386 [R_{int} = 0.0582, R_{sigma} = 0.0806]
Data/restraints/parameters	6386/18/371
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0596, wR_2 = 0.1591
Final R indexes [all data]	R_1 = 0.0846, wR_2 = 0.1772
Largest diff. peak/hole / e Å^{-3}	1.92/-1.99

Table S5 Bond Lengths for {[N{(CF_3)C(2,4,6-$Br_3C_6H_2$)N}$_2$]ZnOEt}$_2$•2(C_6H_6).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zn	Zn^1	2.9222(16)	N3	C1	1.305(9)
Zn	O	1.929(5)	N3	C3	1.441(9)
Zn	O^1	1.969(5)	C1	C9	1.562(11)
Zn	N1	2.041(6)	C2	C10	1.573(10)
Zn	N3	2.030(6)	C3	C4	1.397(11)
Br1	C4	1.899(8)	C3	C8	1.410(11)
Br2	C6	1.898(7)	C4	C5	1.389(11)
Br3	C8	1.875(8)	C5	C6	1.382(12)
Br4	C12	1.903(8)	C6	C7	1.391(12)
Br5	C14	1.880(8)	C7	C8	1.391(11)
Br6	C16	1.885(8)	C11	C12	1.398(11)
F1	C10	1.317(10)	C11	C16	1.416(10)
F2	C10	1.343(10)	C12	C13	1.376(11)
F3	C10	1.309(10)	C13	C14	1.413(11)
F4	C9	1.325(11)	C14	C15	1.379(12)
F5	C9	1.321(10)	C15	C16	1.383(11)

F6	C9	1.342(10)	C18	C19	1.511(13)
O	Zn[1]	1.969(5)	C20	C21	1.373(19)
O	C18	1.430(11)	C20	C25	1.42(2)
N1	C2	1.297(10)	C21	C22	1.395(15)
N1	C11	1.448(10)	C22	C23	1.376(15)
N2	C1	1.337(10)	C23	C24	1.39(2)
N2	C2	1.339(10)	C24	C25	1.33(2)

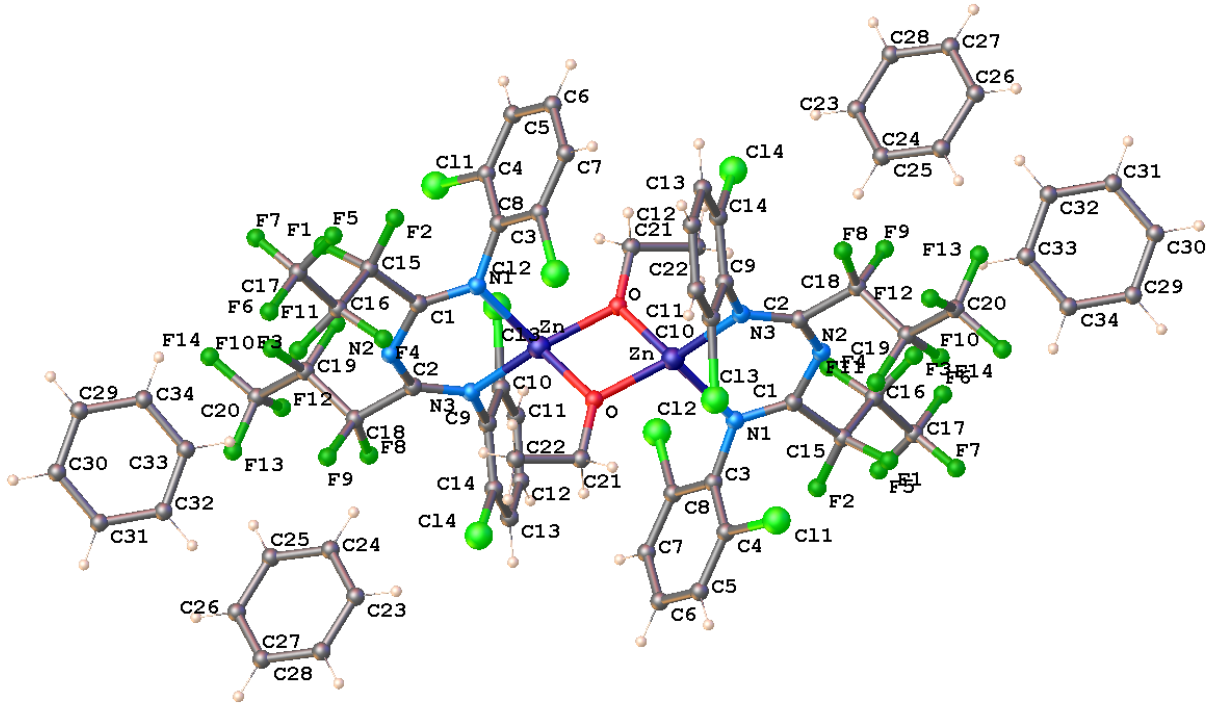
[1]1-X,-Y,1-Z

Table S6 Bond Angles for $\{[N\{(CF_3)C(2,4,6\text{-}Br_3C_6H_2)N\}_2]ZnOEt\}_2 \bullet 2(C_6H_6)$.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O[1]	Zn	Zn[1]	40.91(15)	C3	C8	Br3	122.1(6)
O	Zn	Zn[1]	41.94(15)	C7	C8	Br3	117.1(6)
O	Zn	O[1]	82.9(2)	C7	C8	C3	120.8(8)
O	Zn	N1	118.1(3)	F4	C9	F6	107.0(7)
O[1]	Zn	N1	120.3(2)	F4	C9	C1	112.9(7)
O[1]	Zn	N3	118.5(2)	F5	C9	F4	107.0(8)
O	Zn	N3	125.9(2)	F5	C9	F6	106.4(7)
N1	Zn	Zn[1]	130.60(18)	F5	C9	C1	112.9(7)
N3	Zn	Zn[1]	135.15(17)	F6	C9	C1	110.3(7)
N3	Zn	N1	94.1(2)	F1	C10	F2	106.2(7)
Zn	O	Zn[1]	97.1(2)	F1	C10	C2	115.0(6)
C18	O	Zn	131.1(5)	F2	C10	C2	108.6(7)
C18	O	Zn[1]	131.8(5)	F3	C10	F1	109.7(8)
C2	N1	Zn	118.2(5)	F3	C10	F2	107.8(7)
C2	N1	C11	123.2(6)	F3	C10	C2	109.4(7)
C11	N1	Zn	118.5(5)	C12	C11	N1	122.2(7)
C1	N2	C2	125.5(7)	C12	C11	C16	117.0(7)
C1	N3	Zn	117.9(5)	C16	C11	N1	120.7(7)
C1	N3	C3	121.9(6)	C11	C12	Br4	119.0(6)
C3	N3	Zn	119.3(5)	C13	C12	Br4	118.2(6)
N2	C1	C9	109.7(6)	C13	C12	C11	122.8(7)
N3	C1	N2	130.2(7)	C12	C13	C14	118.6(8)
N3	C1	C9	120.0(7)	C13	C14	Br5	120.1(6)
N1	C2	N2	129.4(7)	C15	C14	Br5	119.8(6)
N1	C2	C10	123.0(7)	C15	C14	C13	120.1(7)
N2	C2	C10	107.6(6)	C14	C15	C16	120.4(7)

C4	C3	N3	120.9(7)	C11	C16	Br6	120.6(6)
C4	C3	C8	117.3(7)	C15	C16	Br6	118.4(5)
C8	C3	N3	121.7(7)	C15	C16	C11	121.0(7)
C3	C4	Br1	118.8(6)	O	C18	C19	113.9(7)
C5	C4	Br1	118.4(6)	C21	C20	C25	119.8(14)
C5	C4	C3	122.7(7)	C20	C21	C22	118.9(13)
C6	C5	C4	118.1(7)	C23	C22	C21	120.8(11)
C5	C6	Br2	120.0(6)	C22	C23	C24	119.3(13)
C5	C6	C7	121.6(7)	C25	C24	C23	121.2(14)
C7	C6	Br2	118.4(6)	C24	C25	C20	119.9(14)
C8	C7	C6	119.4(7)				

[1]1-X,-Y,1-Z



Unit cell of $\{[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]ZnOEt\}_2 \bullet 2(C_6H_6)$, each benzene shown above present at 50% occupancy

Table S7 Crystal data and structure refinement for $\{[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]ZnOEt\}_2 \bullet 2(C_6H_6)$.

Identification code	rad205_0m_a
Empirical formula	$C_{28}H_{17}Cl_4F_{14}N_3OZn$
Formula weight	884.61
Temperature/K	101.58
Crystal system	triclinic
Space group	P-1
a/Å	11.3583(10)
b/Å	12.0545(11)
c/Å	12.6061(11)
α/°	88.972(2)
β/°	79.294(2)
γ/°	87.809(2)
Volume/Å^3	1694.6(3)
Z	2
ρ_{calc}g/cm^3	1.734
μ/mm^{-1}	1.147

F(000)	876.0
Crystal size/mm^3	0.361 × 0.267 × 0.042
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.278 to 51.998
Index ranges	$-14 \leq h \leq 14$, $-14 \leq k \leq 14$, $-15 \leq l \leq 15$
Reflections collected	16822
Independent reflections	6634 [R_{int} = 0.0450, R_{sigma} = 0.0527]
Data/restraints/parameters	6634/144/491
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0530, wR_2 = 0.1423
Final R indexes [all data]	R_1 = 0.0718, wR_2 = 0.1528
Largest diff. peak/hole / e Å^{-3}	2.42/-0.64

Table S8 Bond Lengths for $\{[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]ZnOEt\}_2 \bullet 2(C_6H_6)$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zn	Zn^1	2.9267(8)	C1	C15	1.534(6)
Zn	O	1.929(3)	C2	C18	1.560(5)
Zn	O^1	1.956(3)	C3	C4	1.388(6)
Zn	N1	2.021(3)	C3	C8	1.397(5)
Zn	N3	2.030(3)	C4	C5	1.388(6)
Cl1	C4	1.735(4)	C5	C6	1.381(6)
Cl2	C8	1.730(4)	C6	C7	1.387(6)
Cl3	C10	1.736(4)	C7	C8	1.389(6)
Cl4	C14	1.738(4)	C9	C10	1.398(6)
F1	C15	1.355(5)	C9	C14	1.395(6)
F2	C15	1.356(5)	C10	C11	1.378(6)
F3	C16	1.333(5)	C11	C12	1.382(7)
F4	C16	1.327(6)	C12	C13	1.384(7)
F5	C17	1.305(7)	C13	C14	1.387(6)
F6	C17	1.316(6)	C15	C16	1.529(6)
F7	C17	1.288(8)	C16	C17	1.541(7)
F8	C18	1.335(5)	C18	C19	1.541(6)
F9	C18	1.351(5)	C19	C20	1.540(6)
F10	C19	1.335(5)	C21	C22	1.509(7)
F11	C19	1.344(5)	C23	C24	1.3900
F12	C20	1.310(6)	C23	C28	1.3900
F13	C20	1.330(6)	C24	C25	1.3900
F14	C20	1.321(6)	C25	C26	1.3900

O	Zn[1]	1.956(3)	C26	C27	1.3900
O	C21	1.431(5)	C27	C28	1.3900
N1	C1	1.301(5)	C29	C34	1.3900
N1	C3	1.420(5)	C29	C30	1.3900
N2	C1	1.340(5)	C34	C33	1.3900
N2	C2	1.334(5)	C33	C32	1.3900
N3	C2	1.307(5)	C32	C31	1.3900
N3	C9	1.434(5)	C31	C30	1.3900

[1]1-X,2-Y,1-Z

Table S9 Bond Angles for $\{[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]ZnOEt\}_2 \bullet 2(C_6H_6)$.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O	Zn	Zn[1]	41.47(8)	F1	C15	F2	106.3(3)
O[1]	Zn	Zn[1]	40.78(8)	F1	C15	C1	110.0(3)
O	Zn	O[1]	82.25(12)	F1	C15	C16	108.0(3)
O[1]	Zn	N1	122.29(13)	F2	C15	C1	111.6(3)
O	Zn	N1	111.32(13)	F2	C15	C16	106.1(3)
O	Zn	N3	135.22(13)	C16	C15	C1	114.3(4)
O[1]	Zn	N3	116.93(12)	F3	C16	C15	111.2(4)
N1	Zn	Zn[1]	126.64(9)	F3	C16	C17	104.3(4)
N1	Zn	N3	92.58(12)	F4	C16	F3	109.5(5)
N3	Zn	Zn[1]	140.40(9)	F4	C16	C15	107.9(4)
Zn	O	Zn[1]	97.75(12)	F4	C16	C17	107.8(4)
C21	O	Zn	131.5(2)	C15	C16	C17	115.9(4)
C21	O	Zn[1]	129.0(2)	F5	C17	F6	106.5(5)
C1	N1	Zn	118.3(3)	F5	C17	C16	111.1(5)
C1	N1	C3	124.2(3)	F6	C17	C16	110.9(5)
C3	N1	Zn	117.3(2)	F7	C17	F5	108.1(7)
C2	N2	C1	125.0(3)	F7	C17	F6	108.6(5)
C2	N3	Zn	117.4(3)	F7	C17	C16	111.5(5)
C2	N3	C9	122.9(3)	F8	C18	F9	106.5(3)
C9	N3	Zn	119.5(2)	F8	C18	C2	114.3(3)
N1	C1	N2	127.6(4)	F8	C18	C19	106.6(3)
N1	C1	C15	124.3(3)	F9	C18	C2	108.3(3)
N2	C1	C15	108.1(3)	F9	C18	C19	108.2(3)
N2	C2	C18	106.0(3)	C19	C18	C2	112.7(3)
N3	C2	N2	129.3(3)	F10	C19	F11	109.6(4)

N3	C2	C18	124.7(4)	F10	C19	C18	110.9(4)
C4	C3	N1	121.4(3)	F10	C19	C20	106.1(4)
C4	C3	C8	117.4(3)	F11	C19	C18	107.5(3)
C8	C3	N1	120.9(3)	F11	C19	C20	107.5(4)
C3	C4	Cl1	118.9(3)	C20	C19	C18	115.2(4)
C3	C4	C5	121.9(4)	F12	C20	F13	107.6(4)
C5	C4	Cl1	119.2(3)	F12	C20	F14	108.7(4)
C6	C5	C4	119.3(4)	F12	C20	C19	112.4(4)
C5	C6	C7	120.5(4)	F13	C20	C19	110.1(4)
C6	C7	C8	119.2(4)	F14	C20	F13	107.8(4)
C3	C8	Cl2	118.6(3)	F14	C20	C19	110.2(4)
C7	C8	Cl2	119.8(3)	O	C21	C22	111.0(4)
C7	C8	C3	121.6(4)	C24	C23	C28	120.0
C10	C9	N3	119.7(3)	C23	C24	C25	120.0
C14	C9	N3	123.3(4)	C26	C25	C24	120.0
C14	C9	C10	116.9(4)	C25	C26	C27	120.0
C9	C10	Cl3	118.2(3)	C28	C27	C26	120.0
C11	C10	Cl3	119.7(3)	C27	C28	C23	120.0
C11	C10	C9	122.1(4)	C34	C29	C30	120.0
C10	C11	C12	119.5(4)	C29	C34	C33	120.0
C11	C12	C13	120.2(4)	C32	C33	C34	120.0
C12	C13	C14	119.6(4)	C31	C32	C33	120.0
C9	C14	Cl4	119.3(3)	C32	C31	C30	120.0
C13	C14	Cl4	119.1(3)	C31	C30	C29	120.0
C13	C14	C9	121.6(4)				

[1]1-X,2-Y,1-Z

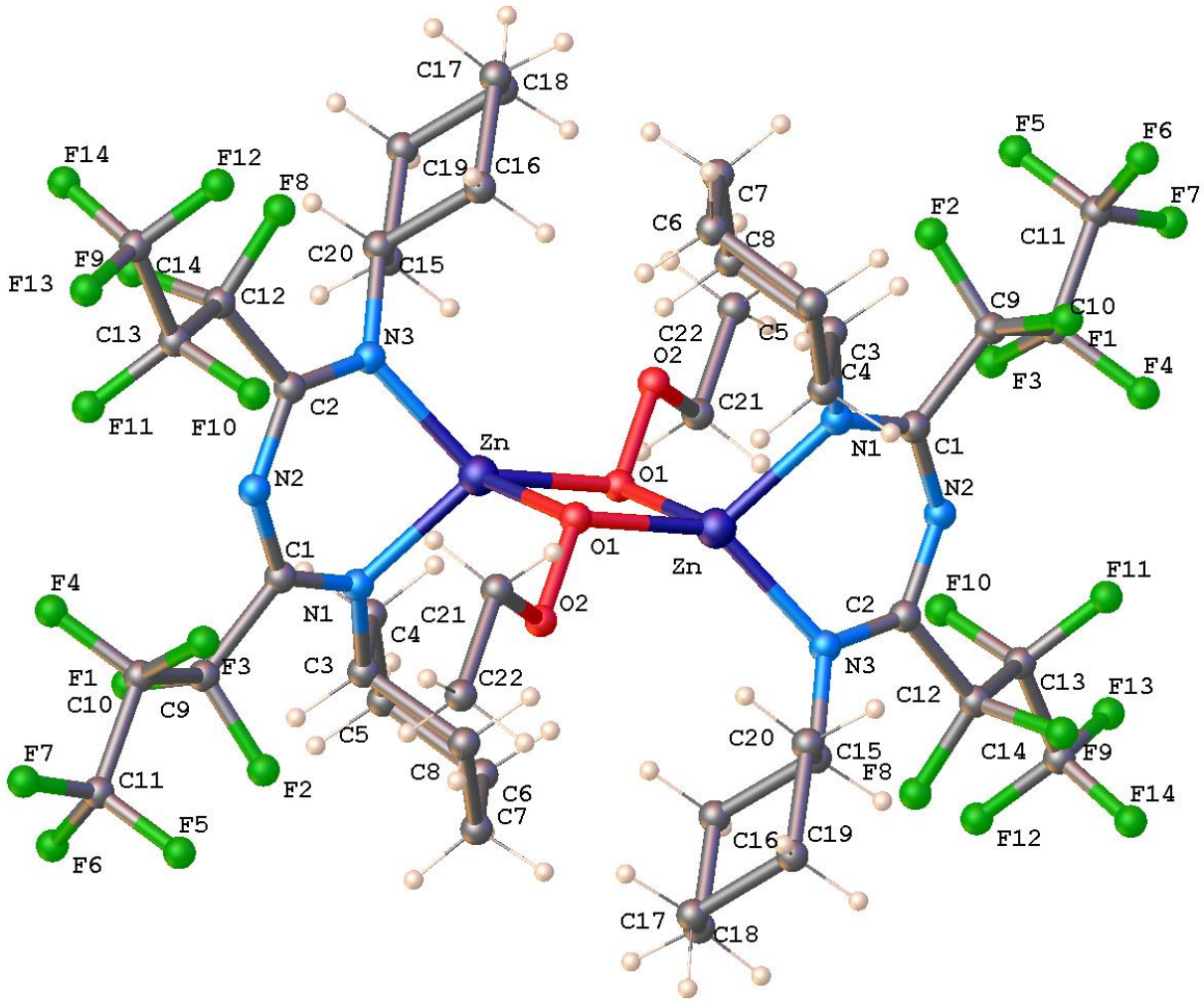


Table S10 Crystal data and structure refinement for {[N{(C_3F_7)C(Cy)N}$_2$]ZnOOEt}$_2$ (**7**).

Identification code	rad157_0m_a
Empirical formula	$C_{44}H_{54}F_{28}N_6O_4Zn_2$
Formula weight	1393.67
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	10.8323(17)
b/Å	11.4141(18)
c/Å	12.2715(19)
α/°	108.695(3)
β/°	96.956(3)

γ/°	96.245(3)
Volume/Å^3	1408.9(4)
Z	1
ρ_{calc}g/cm^3	1.643
μ/mm^{-1}	0.990
F(000)	704.0
Crystal size/mm^3	0.314 × 0.245 × 0.062
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.714 to 56.562
Index ranges	$-14 \leq h \leq 14$, $-15 \leq k \leq 15$, $-16 \leq l \leq 16$
Reflections collected	16540
Independent reflections	6994 [R_{int} = 0.0417, R_{sigma} = 0.0549]
Data/restraints/parameters	6994/0/380
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0434, wR_2 = 0.1075
Final R indexes [all data]	R_1 = 0.0657, wR_2 = 0.1207
Largest diff. peak/hole / e Å^{-3}	1.18/-0.81

Table S11 Bond Lengths for {[N{(C_3F_7)C(Cy)N}$_2$]ZnOOEt}$_2$ (**7**).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zn	Zn^1	3.0474(7)	N2	C1	1.357(3)
Zn	O1^1	2.0487(18)	N2	C2	1.351(3)
Zn	O1	1.9570(17)	N3	C2	1.316(3)
Zn	N1	2.004(2)	N3	C15	1.490(3)
Zn	N3	1.999(2)	C1	C9	1.550(3)
F1	C9	1.375(3)	C2	C12	1.553(3)
F2	C9	1.367(3)	C3	C4	1.540(3)
F3	C10	1.351(3)	C3	C8	1.529(3)
F4	C10	1.346(3)	C4	C5	1.532(3)
F5	C11	1.323(3)	C5	C6	1.537(4)
F6	C11	1.336(3)	C6	C7	1.525(4)
F7	C11	1.334(3)	C7	C8	1.536(3)
F8	C12	1.370(3)	C9	C10	1.550(3)
F9	C12	1.365(3)	C10	C11	1.568(4)
F10	C13	1.350(3)	C12	C13	1.555(4)
F11	C13	1.339(3)	C13	C14	1.565(4)
F12	C14	1.326(3)	C15	C16	1.526(3)

F13	C14	1.340(3)	C15	C20	1.533(4)
F14	C14	1.321(3)	C16	C17	1.526(4)
O1	Zn[1]	2.0487(18)	C17	C18	1.535(4)
O1	O2	1.483(2)	C18	C19	1.523(5)
O2	C21	1.421(3)	C19	C20	1.536(4)
N1	C1	1.307(3)	C21	C22	1.518(4)
N1	C3	1.483(3)			

[1]1-X,1-Y,-Z

Table S12 Bond Angles for $\{[N\{(C_3F_7)C(Cy)N\}_2]ZnOOEt\}_2$ (**7**).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Zn	Zn[1]	41.60(5)	C10	C9	C1	118.0(2)
O1[1]	Zn	Zn[1]	39.36(5)	F3	C10	C9	110.9(2)
O1	Zn	O1[1]	80.96(7)	F3	C10	C11	104.9(2)
O1	Zn	N1	123.80(8)	F4	C10	F3	109.6(2)
O1	Zn	N3	136.02(8)	F4	C10	C9	109.9(2)
N1	Zn	Zn[1]	125.81(6)	F4	C10	C11	107.5(2)
N1	Zn	O1[1]	109.82(8)	C9	C10	C11	113.8(2)
N3	Zn	Zn[1]	138.39(6)	F5	C11	F6	108.6(2)
N3	Zn	O1[1]	115.14(8)	F5	C11	F7	108.2(2)
N3	Zn	N1	90.49(8)	F5	C11	C10	111.2(2)
Zn	O1	Zn[1]	99.04(7)	F6	C11	C10	111.5(2)
O2	O1	Zn[1]	113.42(12)	F7	C11	F6	108.3(2)
O2	O1	Zn	114.30(12)	F7	C11	C10	109.0(2)
C21	O2	O1	106.47(18)	F8	C12	C2	110.8(2)
C1	N1	Zn	114.38(16)	F8	C12	C13	105.2(2)
C1	N1	C3	124.6(2)	F9	C12	F8	106.9(2)
C3	N1	Zn	120.87(15)	F9	C12	C2	110.0(2)
C2	N2	C1	121.9(2)	F9	C12	C13	108.0(2)
C2	N3	Zn	113.91(16)	C2	C12	C13	115.5(2)
C2	N3	C15	124.0(2)	F10	C13	C12	110.0(2)
C15	N3	Zn	122.06(15)	F10	C13	C14	105.7(2)
N1	C1	N2	128.3(2)	F11	C13	F10	109.7(2)
N1	C1	C9	120.4(2)	F11	C13	C12	110.8(2)
N2	C1	C9	111.4(2)	F11	C13	C14	106.0(2)
N2	C2	C12	109.7(2)	C12	C13	C14	114.5(2)

N3	C2	N2	128.8(2)	F12	C14	F13	107.8(2)
N3	C2	C12	121.5(2)	F12	C14	C13	112.2(2)
N1	C3	C4	107.79(19)	F13	C14	C13	108.4(2)
N1	C3	C8	109.84(19)	F14	C14	F12	109.0(2)
C8	C3	C4	110.5(2)	F14	C14	F13	108.3(2)
C5	C4	C3	110.5(2)	F14	C14	C13	111.0(2)
C4	C5	C6	111.3(2)	N3	C15	C16	110.6(2)
C7	C6	C5	111.2(2)	N3	C15	C20	107.80(19)
C6	C7	C8	111.2(2)	C16	C15	C20	110.4(2)
C3	C8	C7	110.9(2)	C15	C16	C17	111.4(2)
F1	C9	C1	109.4(2)	C16	C17	C18	110.9(2)
F1	C9	C10	106.6(2)	C19	C18	C17	111.2(2)
F2	C9	F1	106.80(19)	C18	C19	C20	111.2(3)
F2	C9	C1	109.49(19)	C15	C20	C19	110.7(2)
F2	C9	C10	105.87(19)	O2	C21	C22	106.1(3)

[1]1-X,1-Y,-Z

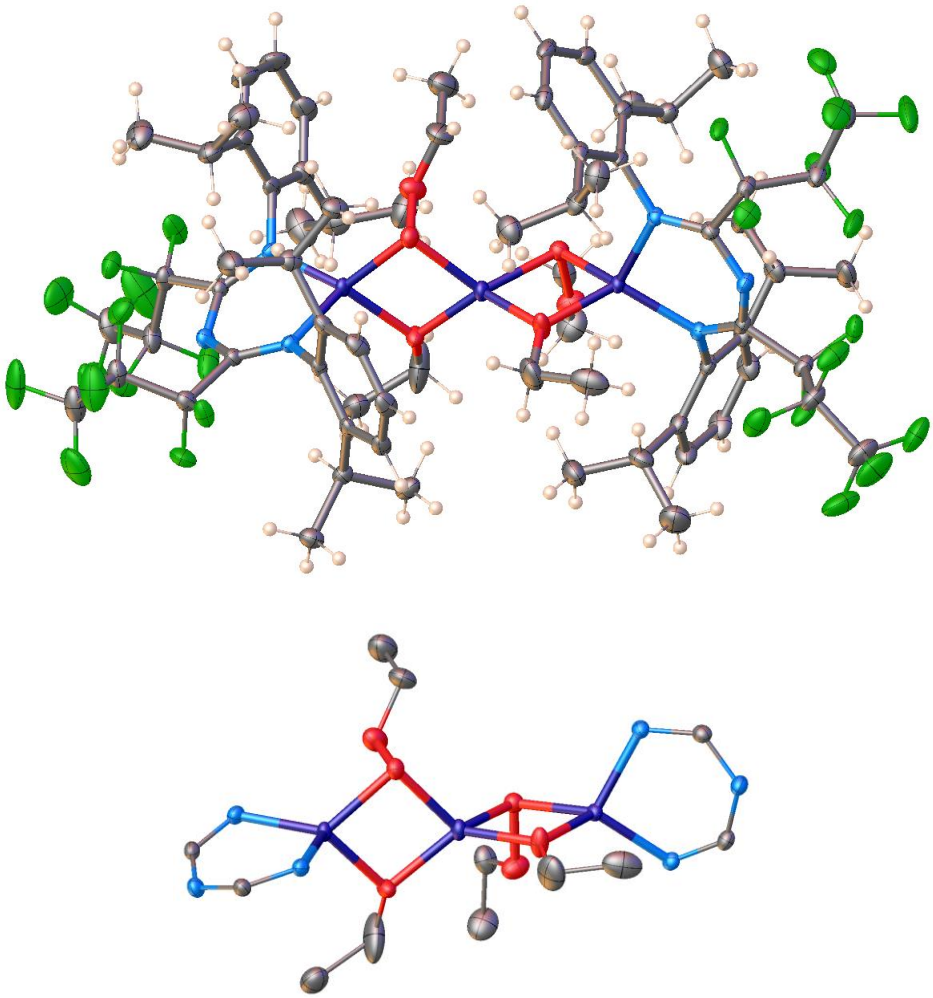


Figure S1. Trinuclear species $\{[N\{(C_3F_7)C(Dipp)N\}_2]Zn(\mu\text{-}OEt)(\mu\text{-}OOEt)\}_2Zn$ obtained from a solution of $[N\{(C_3F_7)C(Dipp)N\}_2]ZnEt$ exposed to dry-air (molecular structure - top; a view of the tri-nuclear core showing ethoxy and ethylperoxy moieties - bottom)

Note: This figure is provided only as supporting information to show the identity of the compound. X-ray data has not been refined to our satisfaction for metrical data comparisons. Compound also did not produce sufficient material for detailed characterization. Nevertheless, the structure shown above is interesting and based on a reasonably well refined dataset. X-ray data show however that it still has a disordered/unaccounted solvent molecule, most likely hexane, in the crystal lattice.

Crystal Data for $C_{75}H_{94}F_{28}N_6O_6Zn_3$ (M =1903.67 g/mol): triclinic, space group P-1 (no. 2), a = 14.5703(13) Å, b = 14.6747(13) Å, c = 22.118(2) Å, α = 97.0720(10)°, β = 101.6260(10)°, γ = 96.9380(10)°, V = 4545.0(7) Å^3, Z = 2, T = 99.99 K, μ(MoKα) = 0.891 mm^{-1}, $Dcalc$ = 1.391 g/cm^3, 39857 reflections measured (5.658° ≤ 2Θ ≤ 50°), 15944 unique (R_{int} = 0.0186, R_{sigma} = 0.0233) which were used in all calculations. The final R_1 was 0.0562 (I > 2σ(I)) and wR_2 was 0.1751 (all data).

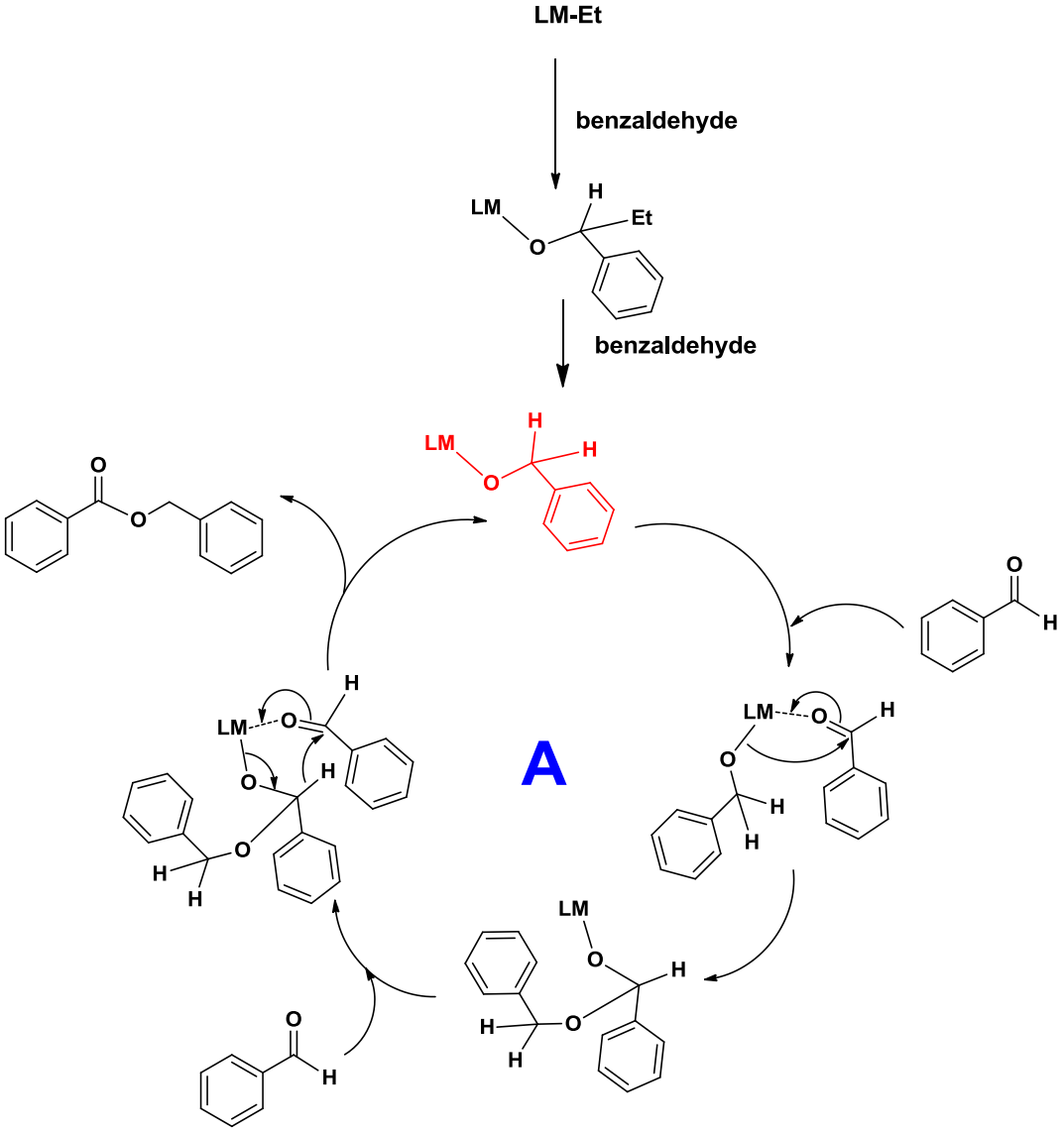


Figure S2. Metal alkoxide catalyzed process adopted for triazapentadienyl ethyl zinc catalyst, which involves the formation of zinc alkoxide from ethyl zinc and aldehyde (see analogous process involving lanthanides: Bürgstein, M. R.; Berberich, H.; Roesky, P. W. *Chem. Eur. J.* **2001**, *7*, 3078-3085).

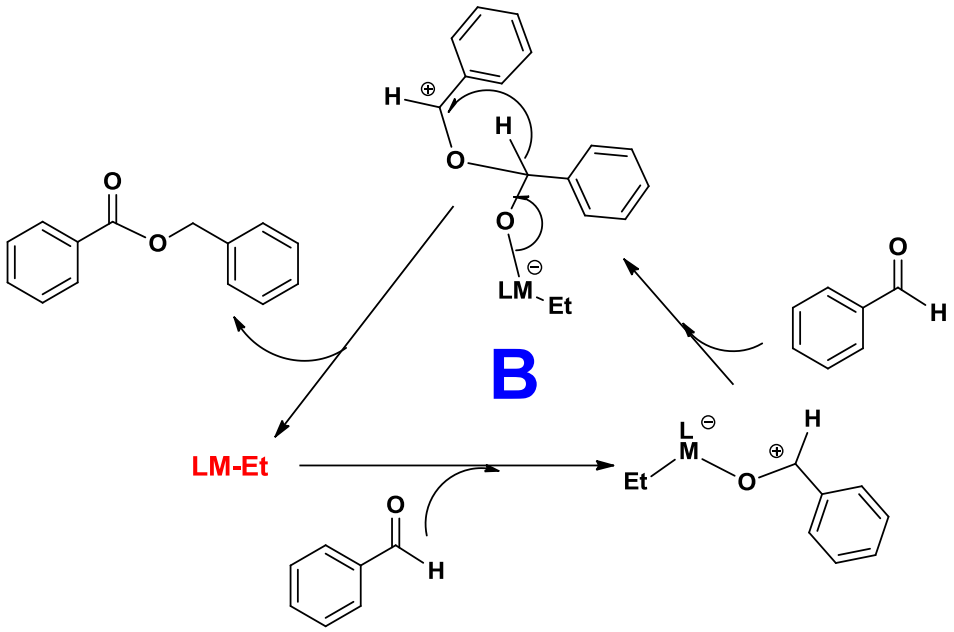


Figure S3. Mechanism proposed by Lin *et al* (Lin, I.; Day, A. R. *J. Am. Chem. Soc.* **1952**, *74*, 5133-5) adopted for triazapentadienyl ethyl zinc catalyst