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

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Ethyl zinc complexes $[N\{(C_3F_7)C(Dipp)N\}_2]ZnEt$, $[N\{(C_3F_7)C(Cy)N\}_2]ZnEt$, $[N\{(CF_3)C(2,4,6\text{-}Br_3C_6H_2)N\}_2]ZnEt$ and $[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]ZnEt$ have been synthesized from the corresponding 1,3,5-triazapentadiene and diethyl zinc. X-ray data show that $[N\{(C_3F_7)C(Dipp)N\}_2]ZnEt$ has a distorted trigonal planar geometry at the zinc center. The triazapentadienyl ligand binds to zinc in a κ^2-mode. The zinc-ethyl bonds of $[N\{(C_3F_7)C(Dipp)N\}_2]ZnEt$, $[N\{(C_3F_7)C(Cy)N\}_2]ZnEt$, $[N\{(CF_3)C(2,4,6\text{-}Br_3C_6H_2)N\}_2]ZnEt$ and $[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]ZnEt$ readily undergo oxygen insertion upon exposure to dry air to produce the corresponding zinc-ethoxy or zinc-ethylperoxy compounds. The ethoxy zinc adducts $\{[N\{(CF_3)C(2,4,6\text{-}Br_3C_6H_2)N\}_2]ZnOEt\}_2$ and $\{[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]ZnOEt\}_2$ as well as the ethylperoxy zinc adduct $\{[N\{(C_3F_7)C(Cy)N\}_2]ZnOOEt\}_2$ have been isolated and fully characterized by several methods including X-ray crystallography. They feature dinuclear structures with four-coordinate zinc sites and bridging-ethoxy or -ethylperoxy groups. The ethyl zinc complexes catalyze the Tishchenko reaction of benzaldehyde under solventless conditions affording benzyl benzoate. The reaction of ethyl zinc complexes with dioxygen and their catalytic behaviour in the Tishchenko reaction are affected by the electronic and steric factors of the triazapentadienyl ligand. $\{[N\{(C_3F_7)C(Cy)N\}_2]ZnOOEt\}_2$ is an excellent reagent for the epoxidation of *trans*-chalcone.

Introduction

1,3,5-Triazapentadienyl systems represent an important class of monoanionic, nitrogen-based ligands.[1] Despite the similarity to the widely used 1,5-diazapentadienyl (β-diketiminate) ligands (Fig. 1),[2,3] they have not received the same attention as metal ion chelators.[1,4–27] 1,3,5-Triazapentadienyl ligands offer a great deal of tunability in their steric and electronic properties. One major area of research focus in our laboratory has been the chemistry of highly fluorinated metal ion chelators[28–30] including polyfluorinated triazapentadienyl ligands. Such ligands are attractive because some of their metal adducts display interesting reactivity and notable improvement in the thermal stability, oxidative resistance, improved volatility and fluorocarbon solubility.[9,31–34]

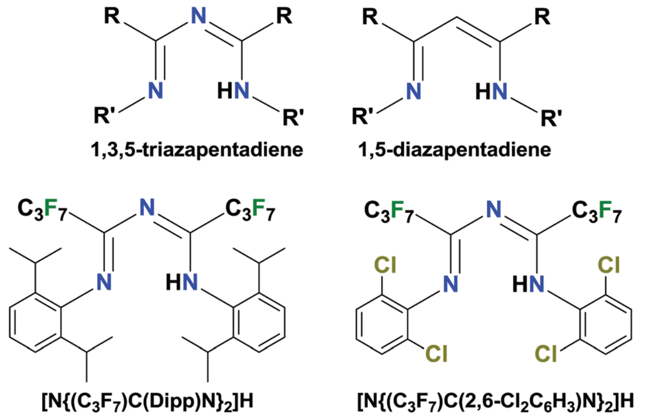

Fig. 1 1,3,5-Triazapentadiene and 1,5-diazapentadiene skeletons (R,R′ = various substituents like alkyl or aryl groups) and sketch of $[N\{(C_3F_7)C(Dipp)N\}_2]H$ and $[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]H$.

We have reported the synthesis of several fluorinated 1,3,5-triazapentadienyl ligands such as $[N\{(C_3F_7)C(Dipp)N\}_2]^-$, $[N\{(C_3F_7)C(Mes)N\}_2]^-$, $[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]^-$ and $[N\{(C_3F_7)$

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$C(C_6F_5)N\}_2]^-$ (Dipp = 2,6-(i-Pr)$_2$C$_6$H$_3$; Mes = 2,4,6-(Me)$_3$C$_6$H$_2$) and their utility in the isolation of metal adducts with interesting bonding and structural features.[7–9,17,31,33,35–40] For example, silver(I) isocyanide adduct *t*-BuNCAg[N{(C$_3$F$_7$)C(Dipp)N}$_2$] features κ^1-bonded triazapentadienyl ligand linked to silver *via* the central nitrogen atom whereas the triphenyl phosphine complex [N{(C$_3$F$_7$)C(C$_6$F$_5$)N}$_2$]Ag(PPh$_3$)$_2$ has a κ^1-bonded triazapentadienyl ligand attached to the metal fragment *via* one of the terminal nitrogen atoms.[8,39] The gold(I) alkene and alkyne adducts [N{(C$_3$F$_7$)C(2,6-Cl$_2$C$_6$H$_3$)N}$_2$]Au(C$_2$H$_4$)[33] and [N{(C$_3$F$_7$)C(Dipp)N}$_2$]Au(EtC≡CEt)[31] feature κ^2-bonded ligand with a U-shaped triazapentadienyl backbones. Tl[N{(C$_3$F$_7$)C(Dipp)N}$_2$] is a mono-coordinate thallium adduct with a W-shaped triazapentadienyl backbone.[17] Some metal complexes of these fluorinated triazapentadienyl ligands exhibit useful catalytic[33,38] and biological activities.[37]

In this article, we describe the synthesis of first mono-(1,3,5-triazapentadienyl) zinc(II) complexes of these fluorinated ligands and some of their chemistry. In particular, we report the isolation of ethyl zinc adducts supported by fluorinated triazapentadienyl ligands, their reactivity towards oxygen leading to ethoxide and ethylperoxide products, and the catalytic applications in Tishchenko reaction, which involves the dimerization of aldehydes to give esters. We also show the oxygen atom transfer chemistry of triazapentadienyl ligand supported zinc ethylperoxide leading to epoxides from olefins.

Results and discussion

The fluoroalkyl substituted triazapentadienes were obtained in excellent yield from the reaction of the perfluoro-aza-alkene with the appropriate amine in ether as depicted in Fig. 2.[5,7–9] The syntheses of [N{(C$_3$F$_7$)C(Dipp)N}$_2$]H[8,9] and [N{(C$_3$F$_7$)C(2,6-Cl$_2$C$_6$H$_3$)N}$_2$]H[33] have been reported while [N{(C$_3$F$_7$)C(Cy)N}$_2$]H and [N{(CF$_3$)C(2,4,6-Br$_3$C$_6$H$_2$)N}$_2$]H were obtained from the reaction of CyNH$_2$ (cyclohexyl amine) with perfluoro-5-aza-4-nonene[5,6,41] or 2,4,6-Br$_3$C$_6$H$_2$NH$_2$ with perfluoro-3-aza-2-pentene,[42] respectively. Triazapentadienes [N{(C$_3$F$_7$)C(Cy)N}$_2$]H and [N{(CF$_3$)C(2,4,6-Br$_3$C$_6$H$_2$)N}$_2$]H were characterized by the solution NMR spectroscopic studies and elemental analyses. These compounds exhibit somewhat complicated ^{1}H, ^{19}F and ^{13}C NMR spectra due to the presence of different conformational isomers and/or tautomers in solution that are close in energy as noted previously for the related systems.[5,6,8]

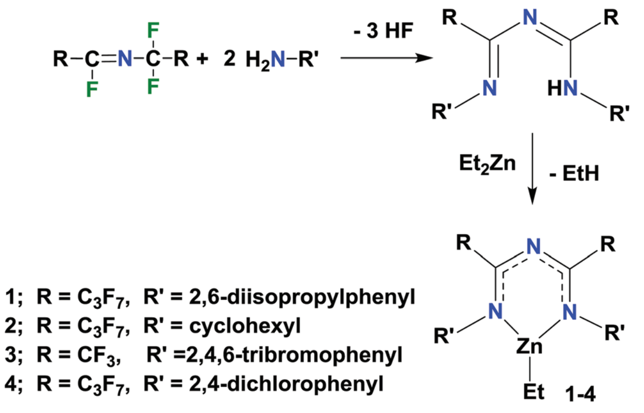


Fig. 2 Synthetic route to triazapentadienes and ethylzinc adducts of triazapentadienyl ligands.

The ethyl zinc adducts **1–4** (Fig. 2) were prepared by heating (~80 °C) a mixture of diethyl zinc and the corresponding 1,3,5-triazapentadiene [N{(C$_3$F$_7$)C(Dipp)N}$_2$]H, [N{(C$_3$F$_7$)C(Cy)N}$_2$]H, [N{(C$_3$F$_7$)C(2,6-Cl$_2$C$_6$H$_3$)N}$_2$]H or [N{(CF$_3$)C(2,4,6-Br$_3$C$_6$H$_2$)N}$_2$]H in toluene. They were obtained in 82–85% yield. The zinc(II) complexes [N{(C$_3$F$_7$)C(Ph)N}$_2$]$_2$Zn and [N{(C$_3$F$_7$)C(H)N}$_2$]$_2$Zn featuring fluorinated triazapentadienyl ligands have been reported but they are bis(1,3,5-triazapentadienyl)zinc adducts.[4,5] Furthermore, no structural data are available for these adducts. The ^{1}H NMR spectrum of [N{(C$_3$F$_7$)C(Dipp)N}$_2$]ZnEt (**1**) in C$_6$D$_6$ displays two doublets for CH(C*H*$_3$)$_2$ and a septet for C*H*(CH$_3$)$_2$ of the isopropyl moieties and a triplet and quartet for the ethyl group. The two doublets for methyl groups of isopropyl moieties are a result of restricted rotation of the aryl and isopropyl groups creating two environments for methyl groups with one set directed at the zinc atom side while second set pointing towards the ligand backbone (see Fig. 3). In the ^{19}F NMR spectrum, only three sets of signals were observed for the two C$_3$F$_7$-groups indicating the C_2-symmetric nature of the triazapentadienyl fragment.

X-ray quality crystals of [N{(C$_3$F$_7$)C(Dipp)N}$_2$]ZnEt (**1**) were obtained from a hexane solution at −10 °C and the structure is

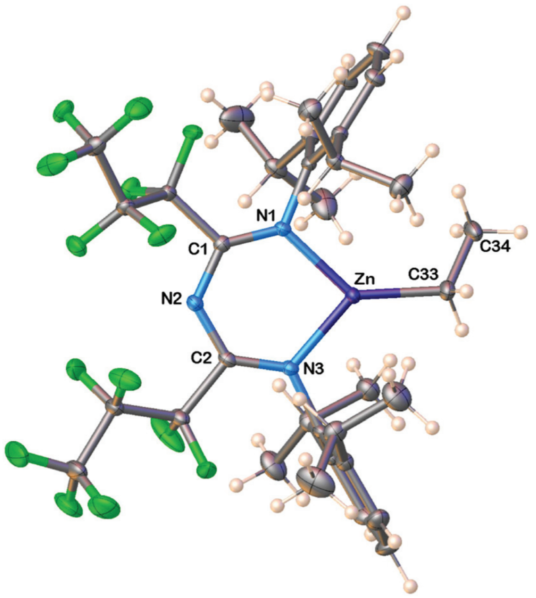


Fig. 3 ORTEP diagram of [N{(C$_3$F$_7$)C(Dipp)N}$_2$]ZnEt (**1**). Selected bond lengths (Å) and angles (°): Zn–N(1) = 1.9931(13), Zn–N(3) = 1.9855(13), Zn–C(33) = 1.9515(16), N(1)–C(1) = 1.301(2), N(2)–C(1) = 1.340(2), N(2)–C(2) = 1.334(2), N(3)–C(2) = 1.306(2), C(1)–C(3) = 1.541(2), C(2)–C(6) = 1.551(2) Å; C(34)–C(33)–Zn = 115.93(12), N(1)–C(1)–N(2) = 128.59(14), C(33)–Zn–(N1) = 133.69(6), C(33)–Zn–(N3) = 133.94(6), N(1)–Zn–N(3) = 92.37(5), C(1)–N(2)–C(2) = 124.99(13)°.

Table 1 Crystal data and summary of data collection and refinement for $[N\{(C_3F_7)C(Dipp)N\}_2]ZnEt$, $\{[N\{(CF_3)C(2,4,6\text{-}Br_3C_6H_2)N\}_2]Zn(\mu\text{-}OEt)\}_2\cdot 2(C_6H_6)$, $\{[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]Zn(\mu\text{-}OEt)\}_2\cdot 2(C_6H_6)$, and $\{[N\{(C_3F_7)C(Cy)N\}_2]Zn(\mu\text{-}OOEt)\}_2$

Compound	$[N\{(C_3F_7)C(Dipp)N\}_2]$-ZnEt	$\{[N\{(CF_3)C(2,4,6\text{-}Br_3C_6H_2)N\}_2]$-$Zn(\mu\text{-}OEt)\}_2\cdot 2(C_6H_6)$	$\{[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]$-$Zn(\mu\text{-}OEt)\}_2\cdot 2(C_6H_6)$	$\{[N\{(C_3F_7)C(Cy)N\}_2]$-$Zn(\mu\text{-}OOEt)\}_2$
Empirical formula	$C_{34}H_{39}F_{14}N_3Zn$	$C_{48}H_{30}Br_{12}F_{12}N_6O_2Zn_2$	$C_{56}H_{34}Cl_8F_{28}N_6O_2Zn_2$	$C_{44}H_{54}F_{28}N_6O_4Zn_2$
Formula weight	821.05	2040.44	1769.22	1393.67
Temperature	100(2) K	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit-cell dimensions	a = 10.2646(6) Å	a = 11.462(2) Å	a = 11.3583(10) Å	a = 10.8323(17) Å
	b = 12.3503(7) Å	b = 11.6254(19) Å	b = 12.0545(11) Å	b = 11.4141(18) Å
	c = 15.2654(8) Å	c = 14.089(2) Å	c = 12.6061(11) Å	c = 12.2715(19) Å
	α = 71.6280(10)°	α = 67.401(3)°	α = 88.972(2)°	α = 108.695(3)°
	β = 86.7850(10)°	β = 89.479(4)°	β = 79.294(2)°	β = 96.956(3)°
	γ = 87.1630(10)°	γ = 63.532(3)°	γ = 87.809(2)°	γ = 96.245(3)°
Volume	1832.65(18) $(Å)^3$	1521.4(4) $(Å)^3$	1694.6(3) $(Å)^3$	1408.9(4) $(Å)^3$
Z	2	1	1	1
Density ρ (calculated)	1.488 $g(cm)^{-3}$	2.227 $g(cm)^{-3}$	1.734 $g(cm)^{-3}$	1.643 $g(cm)^{-3}$
Absorption coefficient μ	0.770 $(mm)^{-1}$	8.748 $(mm)^{-1}$	1.147 $(mm)^{-1}$	0.990 $(mm)^{-1}$
Final R indexes $[I \geq 2\sigma(I)]$	R_1 = 0.0297, wR_2 = 0.0715	R_1 = 0.0596, wR_2 = 0.1591	R_1 = 0.0530, wR_2 = 0.1423	R_1 = 0.0434, wR_2 = 0.1075
Final R indexes [all data]	R_1 = 0.0345, wR_2 = 0.0740	R_1 = 0.0846, wR_2 = 0.1772	R_1 = 0.0718, wR_2 = 0.1528	R_1 = 0.0657, wR_2 = 0.1207

illustrated in Fig. 3 (crystal data are given in Table 1). It reveals a three-coordinate, distorted trigonal planar geometry at the zinc center (with C–Zn–N angles of 133.69(6)°, 133.94(6)° and a 92.37(5)° N–Zn–N angle). The Y-shaped bonding at zinc is similar to those previously reported for copper and silver complexes like $[N\{(C_3F_7)C(Dipp)N\}_2]CuCO$ and $[N\{(C_3F_7)C(Dipp)N\}_2]AgPPh_3$ involving the same ligand.[8,9] The U-shaped ligand backbone is essentially planar and the aromatic rings of "Dipp" moieties are arranged nearly perpendicular to the triazapentadienyl plane (the aromatic rings are twisted by about 90° from the NCNCN plane). The triazapentadienyl ligand binds to the zinc center in a κ^2-mode and the two Zn–N bond lengths are nearly the same (Zn–N = 1.9931(13), 1.9855(13) Å). These bond distances are comparable to the reported Zn–N bond lengths of four-coordinate, triazapentadiene zinc(II) complexes such as $[HN\{(Ph)C(Ph)N\}_2]ZnCl_2$ [43] but are slightly longer than the Zn–N bonds of a related three-coordinate diazapentadienyl ethyl zinc complex $[HC\{(CH_3)C(Dipp)N\}_2]ZnEt$ (Zn–N = 1.979(3) and 1.943(3) Å).[44] Note that $[HC\{(CH_3)C(Dipp)N\}_2]ZnEt$ has a relatively electron rich and better donating supporting ligand than the fluorinated $[N\{(C_3F_7)C(Dipp)N\}_2]^-$. The Zn–C bond distance of $[HC\{(CH_3)C(Dipp)N\}_2]ZnEt$ (1.963(5) Å) is however similar to that of $[N\{(C_3F_7)C(Dipp)N\}_2]ZnEt$ (1.9515(16) Å).

Ethyl zinc complexes **2–4** were characterized by NMR spectroscopy and elemental analyses. The data suggest the formation $[N\{(C_3F_7)C(Cy)N\}_2]ZnEt$ (**2**), $[N\{(CF_3)C(2,4,6\text{-}Br_3C_6H_2)N\}_2]ZnEt$ (**3**) and $[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]ZnEt$ (**4**) featuring rather symmetric κ^2-bound triazapentadienyl ligands as observed in $[N\{(C_3F_7)C(Dipp)N\}_2]ZnEt$ (**1**). For example, the solution NMR data of $[N\{(C_3F_7)C(Cy)N\}_2]ZnEt$ (**2**) in C_6D_6 at room temperature demonstrate the presence triazapentadienyl and ethyl groups at 1 : 1 ratio. The presence of only three set of signals for the two C_3F_7-groups in the ^{19}F NMR spectrum of **2** indicates a C_2-symmetric bonding mode of the ligand.[8,31] The ^1H NMR chemical shift value of methylene protons of the Zn-CH_2CH_3 moiety in complex **2**, which bears *N*-cyclohexyl substituents on the triazapentadienyl ligand is slightly higher (δ 0.55 ppm) compared to the corresponding resonance in complexes **1**, **3** and **4** (δ 0.13, 0.14 and 0.17 ppm, respectively) which have aromatic substituents on the nitrogen. The relative upfield shift of the latter group of signals is probably a result of ring-current effects of flanking arenes. For comparison, the corresponding signal in $[HC\{(CH_3)C(Dipp)N\}_2]ZnEt$ appears at δ 0.24 ppm.[44]

These triazapentadienyl ethyl zinc complexes are sensitive to air and moisture even in the solid form and gradually decompose upon exposure for longer time. Note that reactivity of alkyl zinc compounds with oxygen is not that straight forward and there are even air stable zinc ethyl adducts like $[HB(3,5\text{-}(CF_3)_2Pz)_3]ZnEt$ and $[HB(3\text{-}(t\text{-}Bu)Pz)_3]ZnEt$ in the literature.[45,46] The reaction of triazapentadienyl ethyl zinc complexes **2–4** with dry air under carefully controlled conditions leads to isolable zinc-ethoxide or ethylperoxide derivatives. For example, when toluene solutions of $[N\{(CF_3)C(2,4,6\text{-}Br_3C_6H_2)N\}_2]ZnEt$ (**3**) and $[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]ZnEt$ (**4**) were exposed to an excess of dry air at room temperature (20 °C) for 5 min, and then stored at −20 °C overnight, colourless crystalline precipitates of the corresponding alkoxide $\{[N\{(CF_3)C(2,4,6\text{-}Br_3C_6H_2)N\}_2]Zn(\mu\text{-}OEt)\}_2$ (**5**) and $\{[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]Zn(\mu\text{-}OEt)\}_2$ (**6**) were obtained in about 70% yield (Fig. 4).

Interestingly, the $[N\{(C_3F_7)C(Cy)N\}_2]ZnEt$ (**2**) adduct, in contrast, produced a rare, isolable, zinc-peroxide complex $\{[N\{(C_3F_7)C(Cy)N\}_2]Zn(\mu\text{-}OOEt)\}_2$ (**7**) under the same conditions (Fig. 4). On the other hand, when a toluene solution of $[N\{(C_3F_7)C(Dipp)N\}_2]ZnEt$ (**1**) was exposed to air for a short period of time and then stored at −20 °C, a mixture of compounds were obtained as indicated by the ^1H NMR data of the reaction mixture. We were not been able to isolate analytically

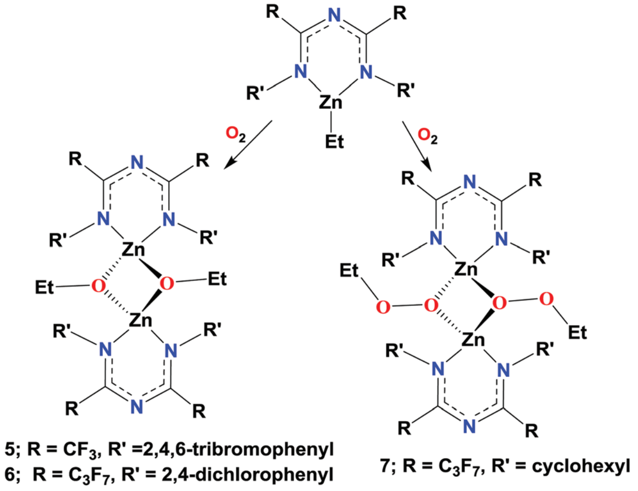


Fig. 4 Synthesis of zinc(II) ethoxide and ethylperoxide adducts from the corresponding ethyl zinc adducts.

pure –ethoxy or –ethylperoxy adducts cleanly thus far from this reaction. One of the reaction mixtures, however produced a crystalline product in low yield, which is a trinuclear species $\{[N\{(C_3F_7)C(Dipp)N\}_2]Zn(\mu\text{-}OEt)(\mu\text{-}OOEt)\}_2Zn$ containing both –ethoxy and –ethylperoxy moieties (see ESI for X-ray structure, Fig. S1†). In all the cases, the air exposure time (should not exceed 5 min) and the storage temperature (−20 °C) were found to be critical to obtain zinc-ethoxide or ethylperoxide adducts in good yield. Longer period of air exposure and room temperature storage leads to the decomposition of the complexes.[47]

The formation of zinc-ethoxy *vs.* zinc-ethylperoxy compound upon oxygen insertion is perhaps governed by the ligand effects. The $[N\{(C_3F_7)C(Cy)N\}_2]^-$ which bears electron donating groups on the nitrogen atoms is a better donor and might be capable of stabilizing the zinc-ethylperoxy complex **7** formed. Whereas $[N\{(CF_3)C(2,4,6\text{-}Br_3C_6H_2)N\}_2]^-$ and $[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]^-$ are relatively weaker donors which drive the reaction towards zinc-ethoxy complexes **5** and **6**. Similar observations are made by Lewiński *et al.*[48] where they have systematically studied the reactions of zinc dialkyls with dioxygen in the presence of different donor ligands. The strong N-donor ligand 4-methylpyridine is found to stabilize the alkylperoxide moiety, while THF, a weaker donor, leads to an alkoxide compound.

The ^1H NMR spectroscopy is very useful in determining the oxygen insertion into the Zn–Et bond. The signal due to zinc-bound methylene protons (Zn-CH_2CH_3) in complexes **3–4** which appears in the range of δ 0.14–0.17 ppm (in C_6D_6) disappears upon exposure to oxygen containing air. A new signal was observed around δ 3.8 ppm (in DMSO-*d6*; these ethoxide compounds are not very soluble in C_6D_6) which is attributable to the –OCH_2–CH_3 moiety, indicating complete oxygenation of the Zn–C bond.

The molecular structures of the zinc-ethoxy complexes $\{[N\{(CF_3)C(2,4,6\text{-}Br_3C_6H_2)N\}_2]Zn(\mu\text{-}OEt)\}_2$ and $\{[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]Zn(\mu\text{-}OEt)\}_2$ are illustrated in Fig. 5 and 6, respectively. They show that $\{[N\{(CF_3)C(2,4,6\text{-}Br_3C_6H_2)N\}_2]Zn(\mu\text{-}OEt)\}_2$ (**5**) and $\{[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]Zn(\mu\text{-}OEt)\}_2$ (**6**) exist as dinuclear aggregates of triazapentadienyl zinc-ethoxy units linked by the μ_2-type bridging of ethoxide groups. These molecules sit on crystallographically imposed centers of inversion. The central $[Zn_2N_4O_2]$ core in both complexes is similar to each other and those observed for the related structurally authenticated diazapentadienyl zinc alkoxides[44,49–59] such as $\{[HC\{(CH_3)C(2,6\text{-}Et_2C_6H_3)N\}_2]Zn(\mu\text{-}OMe)\}_2$ and $\{[HC\{(CH_3)C(Dipp)N\}_2]Zn(\mu\text{-}O^iPr)\}_2$.[44,49] Zinc atoms adopt distorted tetrahedral geometry. The U-shaped N_3C_2-ligand backbone is relatively flat and the aromatic rings on nitrogen atoms are arranged nearly perpendicular to the triazapentadienyl plane. The two zinc atoms are slightly displaced from the triazapentadienyl ligand planes but are co-planar with each-other and with the two bridging oxygen atoms. The Zn⋯Zn separation is similar in **5** and **6** (2.9222(16) and 2.9267(8) Å, respectively). The two Zn–O bond lengths are slightly different both in **5** and **6** (*e.g.*, 1.929(5) and 1.969(5) Å in **5** and 1.929(3) and 1.956(3) Å in **6**) but fall in the typical range observed in other systems (*e.g.*, Zn–O bond lengths of $\{[HC\{(CH_3)C(2,6\text{-}Et_2C_6H_3)N\}_2]Zn(\mu\text{-}OMe)\}_2$ are 1.931(2) and 1.984(2) Å).[44,51]

The IR spectrum (ATR-IR, solid powder) of ethylperoxy derivative $\{[N\{(C_3F_7)C(Cy)N\}_2]Zn(\mu\text{-}OOEt)\}_2$ (**7**) displays a weak absorption band at 853 cm^{-1} which is attributable to the characteristic peroxidic $\tilde{\nu}$(O–O) stretching vibration (for

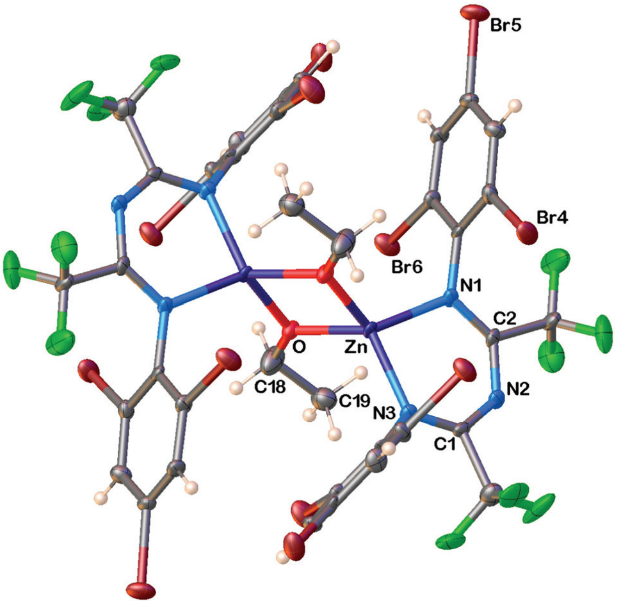


Fig. 5 ORTEP diagram of $\{[N\{(CF_3)C(2,4,6\text{-}Br_3C_6H_2)N\}_2]Zn(\mu\text{-}OEt)\}_2$ (**5**). Selected bond lengths (Å) and angles (°): Zn–N(1) = 2.041(6), Zn–N(3) = 2.030(6), Zn–O = 1.929(5), Zn–O^1 = 1.969(5), N(3)–C(1) = 1.305(9), N(1)–C(2) = 1.297(10), N(2)–C(2) = 1.339(10), N(2)–C(1) = 1.337(10), O–C(18) = 1.430(11), Zn⋯Zn^1 = 2.9222(16) Å; O–Zn–O^1 = 82.9(2), Zn–O–Zn^1 = 97.1(2), N(1)–Zn–O = 118.1(3), N(1)–Zn–O^1 = 120.3(2), N(3)–Zn–O = 125.9(2), N(3)–Zn–O^1 = 118.5(2), N(1)–Zn–N(3) = 94.1(2), N(1)–C(2)–N(2) = 129.4(7), N(2)–C(1)–N(3) = 130.2(7)°.

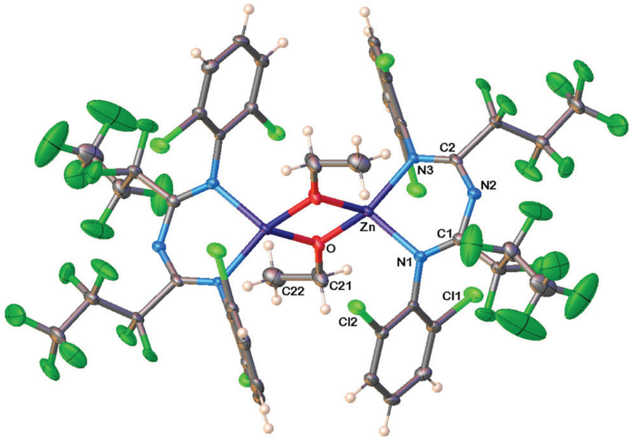
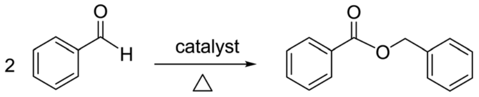


Fig. 6 ORTEP diagram of $\{[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]Zn(\mu\text{-}OEt)\}_2$ (**6**). Selected bond lengths (Å) and angles (°): Zn–N(1) = 2.021(3), Zn–N(3) = 2.030(3), Zn–O = 1.929(3), Zn–O^1 = 1.956(3), N(3)–C(2) = 1.307(5), N(1)–C(1) = 1.301(5), N(2)–C(2) = 1.334(5), N(2)–C(1) = 1.340(5), O–C(21) = 1.431(5), Zn⋯Zn^1 = 2.9267(8) Å; O–Zn–O^1 = 82.25(12), Zn–O–Zn^1 = 97.75(12), N(1)–Zn–O = 111.32(13), N(3)–Zn–O = 135.22(13), N(1)–Zn–O^1 = 122.29(13), N(3)–Zn–O^1 = 116.93(12), N(1)–Zn–N(3) = 92.58(12), N(1)–C(1)–N(2) = 127.6(4), N(2)–C(2)–N(3) = 129.3(3)°.

example, the corresponding band for $\{[HC\{(CH_3)C(Dipp)N\}_2]Zn(\mu\text{-}OOEt)\}_2$ was observed at 854 cm^{-1}).[60] The X-ray crystal structure of **7** is illustrated in Fig. 7. Such isolable and well authenticated alkyl peroxides of zinc are relatively uncommon.[47,48,60–68]

The compound $\{[N\{(C_3F_7)C(Cy)N\}_2]Zn(\mu\text{-}OOEt)\}_2$ (**7**) is a dinuclear species linked by the μ-ethylperoxy groups and sits on a crystallographically imposed center of inversion. The central $[Zn_2O_2]$ core is quite similar to the zinc-ethoxide complexes described above and to the closely related alkylperoxide complex, $\{[HC\{(CH_3)C(Dipp)N\}_2]Zn(\mu\text{-}OOEt)\}_2$.[60] The Zn⋯Zn separation (3.0474(7) Å) and the Zn–O bond lengths (2.0487(18), 1.9570(17) Å) of **7** however, are relatively longer compared to the related distances of ethoxide compounds **5** and **6** but are comparable to the reported 1,5-diazapentadienyl zinc-ethylperoxy complex $\{[HC\{(CH_3)C(Dipp)N\}_2]Zn(\mu\text{-}OOEt)\}_2$. The U-shaped, NCNCN ligand backbone remains relatively planar, while the tetrahedral zinc atom sits above or below the ligand plane forming an envelope-type shape for the ZnNCNCN metallacycle.



The Tishchenko reaction, which involves the dimerization of two aldehydes to form the corresponding carboxylic ester, has been known for nearly a century,[69] and of significant interest to both the industrial and academic scientists due to its atom efficiency and utility.[69,70] During all these years, in addition to the traditional aluminium based catalysts, chemists have investigated new catalytic systems such as those involving alkali[71,72] and alkaline earth metals,[73–75] lanthanides,[76,77] actinides[78,79] and d-block elements[80–83] to mediate Tishchenko chemistry. More recently, the zinc based catalysts have also gained attention for this purpose.[52,73,84] We found that the ethyl zinc complex $[N\{(C_3F_7)C(Dipp)N\}_2]ZnEt$ (**1**) is a very effective catalyst in the dimerization of benzaldehyde, providing the corresponding ester benzyl benzoate, in good yield (Table 2). The catalytic reaction was performed as a solventless process in neat aldehyde using 1 : 100 catalyst : aldehyde molar ratio (25 μmol catalyst : 2.3 mmol aldehyde) at 80 °C for 3 h. The progress of the reaction was monitored by ^{1}H NMR

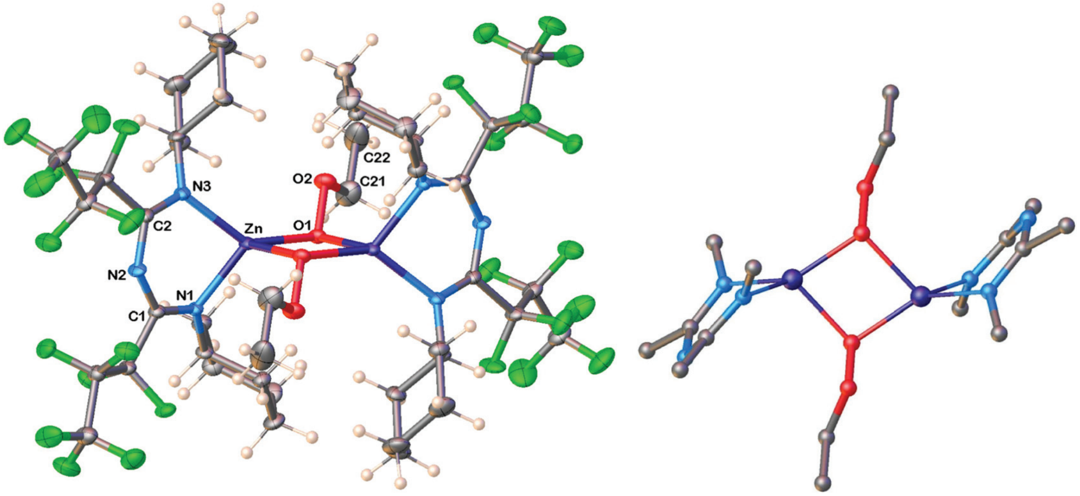


Fig. 7 ORTEP diagram of $\{[N\{(C_3F_7)C(Cy)N\}_2]Zn(\mu\text{-}OOEt)\}_2$ (right) and a view showing the $[ZnOOEt]_2$ core (left). Representative bond lengths (Å) and angles (°): Zn–N(1) = 2.004(2), Zn–N(3) = 1.999(2), Zn–O(1)^1 = 2.0487(18), Zn–O(1) = 1.9570(17), N(3)–C(2) = 1.316(3), N(1)–C(1) = 1.307(3), N(2)–C(2) = 1.351(3), N(2)–C(1) = 1.357(3), O(1)–O(2) = 1.483(2), O(2)–C(21) = 1.421(3), Zn⋯Zn^1 = 3.0474(7) Å; O(1)–Zn–O(1)^1 = 80.96(7), Zn–O(1)–Zn^1 = 99.04(7), N(1)–Zn–O(1) = 123.80(8), N(3)–Zn–O(1) = 136.02(8), N(1)–Zn–O(1)^1 = 109.82(8), N(3)–Zn–O(1)^1 = 115.14(8), N(1)–Zn–N(3) = 90.49(8), N(1)–C(1)–N(2) = 128.3(2), N(2)–C(2)–N(3) = 128.8(2)°.

Table 2 Dimerization of aromatic aldehydes catalysed by ethyl zinc complexes $[N\{(C_3F_7)C(Dipp)N\}_2]ZnEt$ (**1**), $[N\{(C_3F_7)C(Cy)N\}_2]ZnEt$ (**2**), $[N\{(CF_3)C\text{-}(2,4,6\text{-}Br_3C_6H_2)N\}_2]ZnEt$ (**3**) and $[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]ZnEt$ (**4**)

Catalyst	Substrate	Reaction time h	Temp. °C	Yield[a] %
$[N\{(C_3F_7)C(Dipp)N\}_2]ZnEt$	Benzaldehyde	24	20	0
$[N\{(C_3F_7)C(Dipp)N\}_2]ZnEt$	Benzaldehyde	3	50	4
$[N\{(C_3F_7)C(Dipp)N\}_2]ZnEt$	Benzaldehyde	3	80	78
$[N\{(C_3F_7)C(Dipp)N\}_2]ZnEt$	Benzaldehyde	3	110	98
$[N\{(C_3F_7)C(Dipp)N\}_2]ZnEt$	Benzaldehyde	3	140	100
$[N\{(C_3F_7)C(Dipp)N\}_2]ZnEt$	2,3,4,5,6-Pentafluorobenzaldehyde	3	80	36
$[N\{(C_3F_7)C(Dipp)N\}_2]ZnEt$	1-Naphthaldehyde	3	80	60
$[N\{(C_3F_7)C(Cy)N\}_2]ZnEt$	Benzaldehyde	3	80	32
$[N\{(CF_3)C(2,4,6\text{-}Br_3C_6H_2)N\}_2]ZnEt$	Benzaldehyde	3	80	87
$[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]ZnEt$	Benzaldehyde	3	80	66

[a] NMR yields; average of three experiments; also supported by GC-MS analysis.

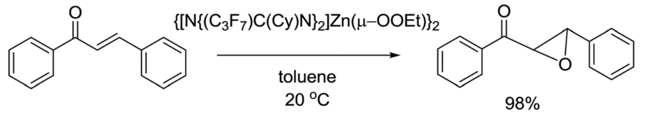
spectroscopy. Gradual disappearance of the aldehyde proton signal (C(O)H; δ = 10.02 ppm) and the appearance of the CH_2 proton resonance of the corresponding ester product (PhC(O)OCH_2Ph) (δ = 5.38 ppm) was noted (in $CDCl_3$). The NMR yield was calculated by integrations of the above mentioned signals.[79,83] Benzyl benzoate was found to be the exclusive product from the reaction mixture, as demonstrated by the NMR and GC/MS analyses, while rest of the aldehyde remained unreacted. The temperature is an important factor in the present catalytic reaction. When the same reaction (catalyst : aldehyde ratio = 1 : 100, reaction time = 3 h) was conducted at room temperature (20 °C), no dimerization was observed and the benzaldehyde remained essentially unreacted, even after extended periods of reaction time (24 h). Subsequently, when the reaction temperature was increased to 50 °C, only about 4% of the product was obtained in 3 h. In contrast, when the reaction temperature was increased to 80, 110 and 140 °C, a significant increase in the aldehyde dimerization was observed, providing products in 78, 98 and 100% yield, respectively (Table 2). This hike in the catalytic activity observed at the higher temperatures (and inactivity or lower activity at the lower temperatures) can be attributed to the high activation energy of the reaction. Longer reaction time at 80 °C (18–20 rather than 3 h) also leads to essentially complete conversion.

The catalytic properties of other ethyl zinc compounds (**2–4**) were also investigated at 80 °C under the similar conditions. The results (Table 2) show a discernible influence of the steric and electronic features of the ligand skeleton on the catalytic ability of these complexes. Noticeably, the other common zinc compounds such as $ZnEt_2$, $ZnCl_2$, $Zn(OAc)_2$ and $Zn(OTf)_2$ did not show significant activity at 80 °C or higher temperatures (*i.e.*, to about 140 °C) under similar conditions (catalyst : benzaldehyde = 1 : 100; reaction time = 3 h). Compared to $[N\{(C_3F_7)C(Dipp)N\}_2]ZnEt$ (**1**), $[N\{(C_3F_7)C(Cy)N\}_2]ZnEt$ (**2**), in which the bulky "Dipp" groups on the nitrogens are replaced by a flexible and less sterically demanding but better donating cyclohexyl groups, exhibits a lower activity giving only 32% of the dimerized product. $[N\{(CF_3)C(2,4,6\text{-}Br_3C_6H_2)N\}_2]ZnEt$ (**3**), in contrast, produced the aldehyde dimerization product in 87% yield under similar conditions. Although it is tempting to attribute the lower and higher reactivity of the latter two systems compared to that of **1** to the changes in Lewis-acidity of the zinc center (which would affect the aldehyde coordination), the good activity of $[HC\{(CH_3)C(Dipp)N\}_2]ZnEt$ (which contains a non-fluorinated diazapentadienyl ligand) in Tishchenko chemistry points to more complex ligand effects.[52] Lower activity of less sterically protected triazapentadienyl zinc adducts could also be a result of the coordination of more than one aldehyde (or Lewis base) to the zinc site affecting the acidity.[85] In fact, studies involving aluminium alkoxides suggest two different rate-determining steps for bulky alkoxide and less-bulky alkoxide containing catalysts (*i.e.*, the rate determining step is the coordination of aldehyde for the former while the hydride-shift from alkoxide for the latter).[86] Furthermore, *t*-BuOCuL catalyzed processes show that electron donating ligands (L) provide higher activity in the benzaldehyde to benzyl benzoate conversion (*t*-BuOCu alone is inactive).[69,87]

These triazapentadienyl-zinc ethyl complexes can also efficiently catalyse the dimerization other aldehydes apart from benzaldehyde. For example, $[N\{(C_3F_7)C(Dipp)N\}_2]ZnEt$ (**1**) can catalyse the dimerization of 2,3,4,5,6-pentafluorobenzaldehyde and 1-naphthaldehyde to give the corresponding esters, perfluorobenzyl 2,3,4,5,6-pentafluorobenzoate (36%) and naphthalen-2-ylmethyl 2-naphthoate (60%) in moderate yields under similar reaction conditions. In the case of acetaldehyde, a mixture of compounds including the expected dimer (ethyl acetate) and other oligomers was obtained.[70,88]

Although we have not explored the mechanism in detail, it is possible to speculate various options based on the results of this study and literature data. A widely used mechanism proposed for the Tishchenko reaction involves metal-alkoxides as key intermediates in the catalytic reaction (see ESI, Fig. S2†).[69,76] Furthermore, some studies have also reported an equal catalytic activity for the metal-alkyl and the corresponding metal-alkoxy complexes.[79] Accordingly, zinc-ethoxide complexes $\{[N\{(CF_3)C(2,4,6\text{-}Br_3C_6H_2)N\}_2]Zn(\mu\text{-}OEt)\}_2$ (**5**) and

$\{[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]Zn(\mu\text{-}OEt)\}_2$ (**6**) we have obtained from the oxygen insertion reaction may also facilitate the dimerization of benzaldehyde. However, to our surprise, **5** and **6** and the ethylperoxy complex $\{[N\{(C_3F_7)C(Cy)N\}_2]Zn(\mu\text{-}OOEt)\}_2$ (**7**) did not produce benzyl benzoate from benzaldehyde even at higher temperatures 100–140 °C and longer reaction time (24 h). This inactivity is may be due to the dimeric nature (Fig. 5–7) of the zinc-alkoxide/peroxide complexes. The steric constraints caused by the crowded environment at zinc of these dimeric species might prevent the effective coordination of the incoming aldehyde to the zinc center, hence impeding the catalytic process. Yet another mechanism used commonly for the Tishchenko reaction is the one first proposed by Lin *et al.* for aluminium alkoxides, which involve a direct hydride shift between aldehydes facilitated by a Lewis acidic metal site.[69,89] This route does not alter the ligands originally on the catalyst (see ESI, Fig. S3†). In fact, a reaction between $[N\{(C_3F_7)C(Dipp)N\}_2]ZnEt$ (**1**, 0.2 mmol) and benzaldehyde (0.5 mmol) (*i.e.*, catalyst : aldehyde molar ratio of 1 : 2.5) in hexane at 60 °C for 3 h afforded benzyl benzoate quantitatively while the zinc ethyl complex **1** remained essentially unchanged (no zinc-alkoxide moiety was detected in the ^1H NMR spectrum). Similar observation was also noted in a closely related study involving diazapentadienyl zinc-ethyl complexes $[HC\{(CH_3)C(2,6\text{-}Et_2C_6H_3)N\}_2]ZnEt$ and $[HC\{(CH_3)C(Dipp)N\}_2]ZnEt$.[52] Thus a later mechanism involving zinc-alkyl catalysts is a valid option for these catalysts although we cannot rule out alkoxide pathway mediated by small quantities of zinc alkoxide species (that could generate under reaction conditions) without data from additional studies.



The epoxidation of electron-deficient olefins is an important process in organic chemistry, and the zinc alkylperoxides are believed to be promising reagents for this reaction.[60,64] The well defined $\{[N\{(C_3F_7)C(Cy)N\}_2]Zn(\mu\text{-}OOEt)\}_2$ (**7**) we have isolated may be a good reagent for this process. Indeed, when it was treated with an equimolar amount of *trans*-chalcone at 20 °C in toluene, the epoxidation product, phenyl(3-phenyloxiran-2-yl)methanone was obtained in quantitative yield in 15 min. This indicates an outstanding oxidizing ability of **7**.

Summary and conclusions

We have successfully prepared a series of zinc ethyl complexes supported by fluoroalkyl substituted triazapentadienyl ligands. The zinc-ethyl bonds of these adducts are sensitive towards oxygen and undergo oxygen insertion leading to the corresponding zinc-ethoxy or zinc-ethylperoxy compounds within few minutes. Prolonged exposure to air at room temperature causes decomposition. These zinc-ethyl complexes serve as good catalysts in the Tishchenko reaction of benzaldehyde under solventless conditions, whereas the corresponding oxygenated, dinuclear complexes remain inactive. A rare zinc-ethylperoxo compound has also been isolated and fully characterized and successfully employed in epoxidation of *trans*-chalcone. Additional studies on metal mediated Tishchenko reaction as well as the oxidation chemistry of zinc alkylperoxy adducts are in progress.

Experimental

All manipulations were carried out under an atmosphere of purified dry nitrogen using standard Schlenk techniques or in a MBRAUN LABMaster glove-box equipped with a −10 °C refrigerator. Solvents were purchased from commercial sources, purified by distilling over conventional drying agents or by using Innovative Technology SPS-400 PureSolv solvent drying system and degassed by the freeze–pump–thaw method prior to use. Glassware was oven-dried at 150 °C overnight. NMR spectra were recorded on a JEOL Eclipse 500. Proton and carbon chemical shifts are reported in ppm, and referenced using the residual proton or carbon signals of the deuterated solvent. ^{19}F NMR chemical shifts were referenced relative to $CFCl_3$ (external). Elemental analyses were performed at Intertek Pharmaceutical Services, Whitehouse, NJ. The precursors for the ligands, perfluoro-5-aza-4-nonene[5,6] and perfluoro-3-aza-4-pentene,[42] and the ligands $[N\{(C_3F_7)C(Dipp)_2C_6H_3)N\}_2]H$[8,9] and $[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]H$[33,37] were prepared by using the published procedure. Rest of the materials used in this work were obtained from commercial vendors (mainly Sigma Aldrich) and used without further purification unless otherwise stated. The products of the catalytic processes were identified by NMR studies by comparison with previously reported data or commercial samples.[60,79,83,90]

Synthesis of $[N\{(C_3F_7)C(Cy)N\}_2]H$

Perfluoro-5-aza-4-nonene (5.41 g, 12.5 mmol) was added dropwise to a solution of cyclohexylamine (6.23 g, 63 mmol) in diethylether (30 mL) at 0 °C. The solution was allowed to stir overnight at room temperature. The resulting mixture was filtered, the filtrate was collected and washed first with 10% HCl (30 mL) and then twice with distilled water (30 mL × 2). The ether layer was separated and dried over $CaCl_2$. The solvent was removed under reduced pressure and the resulting residue was recrystallized from hexane at 0 °C to obtain the colourless crystals of $[N\{(C_3F_7)C(Cy)N\}_2]H$. Yield 70%. M.P. 58–60 °C. ^1H NMR ($CDCl_3$, 500.16 MHz, 298 K): δ 1.10 to 1.95 (several overlapping peaks, br and sharp, 20H, CH_2), 3.13 and 3.53 (m, 2H, *ipso* Cy). 5.27 (br, 1H, N*H*). ^{19}F NMR ($CDCl_3$, 470.62 MHz, 298 K): −80.39 (t, J = 9.1 Hz, CF_3), −80.53 (t, J = 9.1 Hz, CF_3), −115.35 and −117.37 (AB multiplet, J_{AB} = 264 Hz, α-CF_2), −115.86 (br, α-CF_2), −125.45 (s, β-CF_2), −125.57 (s, β-CF_2), −126.60 (s, β-CF_2). ^{13}C NMR ($CDCl_3$, 125.77 MHz, 298 K): δ 24.5, 25.0, 25.6, 31.2, 32.9, 33.5, 51.0, 58.6, 105.0–125.0 (m, $CF_2CF_2CF_3$), 141.0 (t, J = 26.3 Hz, N*C*N), 146.4 (t, J = 26.3 Hz, N*C*N). Anal. Calcd for $\mathrm{C_{20}H_{23}F_{14}N_3}$: C, 42.04; H, 4.06; N, 7.35%. Found: C, 42.19; H, 3.88; N, 7.19%.

$\mathrm{[N\{(CF_3)C(2,4,6\text{-}Br_3C_6H_2)N\}_2]H}$

Perfluoro-3-aza-2-pentene (2.91 g, 12.5 mmol) was added dropwise to a solution of trimethylamine (3.78 g, 37.5 mmol) and 2,4,6-tribromoaniline (8.22 g, 25 mmol) in ether at 0 °C (30 mL). The solution was allowed to stir overnight at room temperature. The resulting mixture was filtered, the filtrate was collected and washed first with 10% HCl (30 mL) and then twice with distilled water (30 mL × 2). The ether layer was separated and dried over $\mathrm{CaCl_2}$. The solvent was removed under reduced pressure and the resulting residue was recrystallized from hexane at 0 °C to obtain the desired ligand as a light yellow solid. Yield 75%. M.P. 155–157 °C. ^{1}H NMR ($\mathrm{CDCl_3}$, 500.16 MHz, 298 K): δ 6.62 (s, 1H, N*H*), 7.59 and 7.79 (s, 4H, *m*-Ar). ^{19}F NMR ($\mathrm{CDCl_3}$, 470.62 MHz, 298 K): −80.03 and −79.50 (s, $\mathrm{C}F_3$). ^{13}C NMR ($\mathrm{CDCl_3}$ 125.77 MHz, 298 K): δ 109.5 (q, *J* = 273.5 Hz, $C\mathrm{F_3}$) 117.2 (q, *J* = 273.5 Hz, $C\mathrm{F_3}$), 117.3, 124.0, 125.0, 132.0, 134.4, 135.0 (Ar), 141.1 (q, *J* = 29.9 Hz, N*C*N), 147.5 (q, *J* = 29.9 Hz, N*C*N). Anal. Calcd for $\mathrm{C_{16}H_5Br_6F_6N_3}$: C, 23.08; H, 0.61; N, 5.05%. Found: 23.44, 0.38, 4.04%.

General procedure for synthesis of ethyl zinc complexes (1–4)

Diethyl zinc (1 M solution in toluene/hexane, 0.41 mmol, 1.5 eq.) was added to a solution of 1,3,5-triazapentadiene (0.27 mmol) in toluene (~5 mL) at room temperature. The resulting clear solution was heated at 80 °C for 48–72 h in a sealed tube. The reaction mixture was cooled down to room temperature and the volatiles were removed under reduced pressure. Ethyl zinc complexes were obtained as colorless to light yellow solids. These ethyl zinc complexes (**1–4**) are soluble in common solvents like hexane, toluene, benzene, THF, chloroform and dichloromethane.

$\mathrm{[N\{(C_3F_7)C(Dipp)N\}_2]ZnEt}$ (1). Pale-yellow solid. Yield 82%. The X-ray quality colorless crystals were obtained from a hexane solution kept at −10 °C overnight. ^{1}H NMR ($\mathrm{C_6D_6}$, 500.16 MHz, 298 K): δ 0.13 (q, 2H, *J* = 8.0 Hz, $\mathrm{C}H_2\mathrm{CH_3}$), 0.59 (t, 3H, *J* = 8.0 Hz, $\mathrm{CH_2C}H_3$), 1.14 (d, *J* = 6.9 Hz, 12H, $\mathrm{CH(C}H_3)_2$), 1.18 (d, *J* = 6.9 Hz, 12H, $\mathrm{CH(C}H_3)_2$), 3.04 (sept, *J* = 6.9 Hz, 4H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 6.96–7.10 (m, 6H, *m*-and *p*-Ar). ^{19}F NMR ($\mathrm{C_6D_6}$, 470.62 MHz, 298 K): δ −80.39 (t, *J* = 11.0 Hz, 6F, $\mathrm{CF_3}$), −106.26 (q, *J* = 11.0 Hz, 4F, α-$\mathrm{CF_2}$), −121.97 (br, 4F, β-$\mathrm{CF_2}$). ^{13}C NMR ($\mathrm{C_6D_6}$, 125.77 MHz, 298 K): δ −0.09 (s, $C\mathrm{H_2CH_3}$), 10.7 (s, $\mathrm{CH_2}C\mathrm{H_3}$), 23.0, 24.3 (s, $\mathrm{CH(}C\mathrm{H_3)_2}$), 29.0 (s, $C\mathrm{H(CH_3)_2}$), 105.0–125.0 (m, $C\mathrm{F_2}C\mathrm{F_2}C\mathrm{F_3}$), 127.8, 128.0, 139.3, 139.9 (Ar), 155.4 (t, *J* = 23.7 Hz, N*C*N). Anal. Calcd for $\mathrm{C_{34}H_{39}N_3F_{14}Zn}$: C, 49.74; H, 4.79; N, 5.12%. Found: C, 49.05; H, 4.01; N, 4.86%.

$\mathrm{[N\{(C_3F_7)C(Cy)N\}_2]ZnEt}$ (2). Colorless solid. Yield 80%. ^{1}H NMR ($\mathrm{C_6D_6}$, 500.16 MHz, 298 K): δ 0.55 (q, 2H, *J* = 8.0 Hz, $\mathrm{C}H_2\mathrm{CH_3}$), 1.39 (t, 3H, *J* = 8.0 Hz, $\mathrm{CH_2C}H_3$), 0.99, 1.29, 1.51 (m, 20H, Cy), 3.71 (m, 2H, *ipso*Cy).^{19}F NMR ($\mathrm{C_6D_6}$, 470.62 MHz, 298 K): δ −80.01 (t, *J* = 11.0 Hz, 6F, $\mathrm{C}F_3$), −105.79 (q, *J* = 11.0 Hz, 4F, α-$\mathrm{C}F_2$), −123.68 (br, 4F, β-$\mathrm{C}F_2$). ^{13}C NMR ($\mathrm{C_6D_6}$, 125.77 MHz, 298 K): δ 6.6 (s, $C\mathrm{H_2CH_3}$), 12.2 (s, $\mathrm{CH_2}C\mathrm{H_3}$), 24.8, 24.9, 35.1, 59.4, 105.0–125.0 (m, $C\mathrm{F_2}C\mathrm{F_2}C\mathrm{F_3}$), 153.3 (t, *J* = 23.9 Hz, N*C*N). Anal. Calcd for $\mathrm{C_{22}H_{27}F_{14}N_3Zn}$: C, 39.74; H, 4.09; N, 6.32%. Found: C, 40.89; H, 3.73; N, 6.04%.

$\mathrm{[N\{(CF_3)C(2,4,6\text{-}Br_3C_6H_2)N\}_2]ZnEt}$ (3). Pale-yellow solid. Yield 85%. ^{1}H NMR ($\mathrm{C_6D_6}$, 500.16 MHz, 298 K): δ 0.14 (q, 2H, *J* = 8.0 Hz, $\mathrm{C}H_2\mathrm{CH_3}$), 0.73 (t, 3H, *J* = 8.0 Hz, $\mathrm{CH_2C}H_3$), 7.19 (s, 4H, *m*-Ar). ^{19}F NMR ($\mathrm{C_6D_6}$, 470.62 MHz, 298 K): δ −67.27 (s, $\mathrm{CF_3}$). ^{13}C NMR ($\mathrm{C_6D_6}$ 125.77 MHz, 298 K): δ −2.2 (s, $C\mathrm{H_2CH_3}$), 10.8 (s, $\mathrm{CH_2}C\mathrm{H_3}$), 117.2 (q, *J* = 273.5 Hz, $C\mathrm{F_3}$), 119.0, 120.3, 134.4, 141.5 (Ar), 157.2 (q, *J* = 31.5 Hz, N*C*N). Anal. Calcd for $\mathrm{C_{18}H_9Br_6F_6N_3Zn}$: C, 23.34; H, 0.98; N, 4.54%. Found: C, 22.95; H, 0.93; N, 4.31%.

$\mathrm{[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]ZnEt}$ (4). Pale-yellow solid. Yield 82%. ^{1}H NMR ($\mathrm{C_6D_6}$, 500.16 MHz, 298 K): δ 0.17 (q, 2H, *J* = 8.0 Hz, $\mathrm{C}H_2\mathrm{CH_3}$), 0.71 (t, 3H, *J* = 8.0 Hz, $\mathrm{CH_2C}H_3$), 6.21 (t, 2H, *J* = 8.0 Hz, *p*-Ar), 6.72 (d, 4H, *J* = 8.0 Hz, *m*-Ar). ^{19}F NMR ($\mathrm{C_6D_6}$, 470.62 MHz, 298 K): δ −80.40 (apparent triplet, *J* = 11.0 and 7.3 Hz, 6F, $\mathrm{C}F_3$), −109.89 (apparent quartet, *J* = 10.9 Hz, 4F, α-$\mathrm{C}F_2$), −122.66 (br, 4F, β-$\mathrm{C}F_2$).^{13}C NMR ($\mathrm{C_6D_6}$, 125.77 MHz, 298 K): δ −2.4 (s, $\mathrm{C}H_2\mathrm{CH_3}$), 10.5 (s, $\mathrm{CH_2C}H_3$), 105.0–125.0 (m, $C\mathrm{F_2}C\mathrm{F_2}C\mathrm{F_3}$), 122.7, 127.6, 129.4, 139.6 (Ar), 156.5 (t, *J* = 24.5 Hz, N*C*N). Anal. Calcd for $\mathrm{C_{22}H_{11}Cl_4F_{14}N_3Zn}$: C, 33.42; H, 1.40; N, 5.32%. Found: C, 32.92; H, 1.54; N, 4.85%.

General procedure for the synthesis of ethoxy- or ethylperoxy-zinc complexes

The ethyl zinc complex (**2–4**) (0.25 mmol) was placed in a Schlenk flask and dry toluene/benzene (~10 mL) was added. Resulting solution was stirred under the positive pressure of dry air for 5 min at 20 °C. Then the Schlenk flask was sealed and placed in freezer at −20 °C overnight to obtain the corresponding ethoxy- (**5** or **6**) or ethylperoxy (**7**) complex as colorless to pale yellow crystalline materials. These adducts are less soluble in solvents like hexane, benzene, chloroform and dichloromethane but show good solubility in DMSO.

$\mathrm{\{[N\{(CF_3)C(2,4,6\text{-}Br_3C_6H_2)N\}_2]Zn(\mu\text{-}OEt)\}_2}$ (5). Light yellow solid. Yield 71%. ^{1}H NMR (DMSO-d6, 500.16 MHz, 298 K): δ 1.07 (t, 6H, *J* = 6.9 Hz, $\mathrm{OCH_2C}H_3$), 3.83 (q, 4H, *J* = 6.9 Hz, $\mathrm{OC}H_2\mathrm{CH_3}$), 7.33 (s, 8H, *m*-Ar). ^{19}F NMR (DMSO-d6, 470.62 MHz, 298 K): δ −68.04 (s, $\mathrm{C}F_3$). ^{13}C NMR (DMSO-d6, 125.77 MHz, 298 K): δ 13.7 (s, $\mathrm{OCH_2}C\mathrm{H_3}$), 71.4 (s, $\mathrm{O}C\mathrm{H_2CH_3}$), 119.1 (q, *J* = 285.1 Hz, $C\mathrm{F_3}$), 117.9, 128.8, 133.6, 148.7 (Ar), 147.58 (q, *J* = 32.5 Hz, N*C*N). Anal. Calcd for $\mathrm{C_{36}H_{18}Br_{12}F_{12}N_6O_2Zn_2}$: C, 22.95; H, 0.96; N, 4.46. Found: C, 22.15; H, 0.83; N, 4.13%.

$\mathrm{\{[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]Zn(\mu\text{-}OEt)\}_2}$ (6). Pale-yellow solid. Yield 72%. ^{1}H NMR (DMSO-d6, 500.16 MHz, 298 K): δ 1.07 (t, 3H, *J* = 6.9 Hz, $\mathrm{CH_2C}H_3$), 3.83 (q, 2H, *J* = 6.9 Hz, $\mathrm{C}H_2\mathrm{CH_3}$), 6.78 (t, 2H, *J* = 8.0 Hz, *p*-Ar), 7.14 (d, 4H, *J* = 8.0 Hz, *m*-Ar). ^{19}F NMR (DMSO-d6, 470.62 MHz, 298 K): δ −79.52 (apparent triplet, *J* = 11.0 and 7.3 Hz, 12F, $\mathrm{C}F_3$), −111.35 (b, 8F, α-$\mathrm{C}F_2$), −123.99 (br, 8F, β-$\mathrm{C}F_2$). ^{13}C NMR (DMSO-d6, 125.77 MHz, 298 K): δ 13.7 (s, $\mathrm{OCH_2}C\mathrm{H_3}$), 71.4 (s, $\mathrm{O}C\mathrm{H_2CH_3}$), 105.0–121.0 (m, $C\mathrm{F_2}C\mathrm{F_3}C\mathrm{F_3}$), 122.7, 125.8, 128.7, 139.4 (Ar), 146.5 (t, *J* = 25.0 Hz, N*C*N). Anal. Calcd for $\mathrm{C_{44}H_{22}Cl_8F_{28}N_6O_2Zn_2}$, C, 32.76; H, 1.37; N, 5.21%. Found: 32.11, H 1.20, N 4.92%.

$\{[N\{(C_3F_7)C(Cy)N\}_2]Zn(\mu\text{-}OOEt)\}_2$ (7). Colorless solid. Yield 70%. ^{1}H NMR (DMSO-d6, 500.16 MHz, 298 K): δ 1.20, 1.69 1.90 (m, 40H, Cy), 1.23 (t, 6H, J = 6.9 Hz, $OOCH_2CH_3$), 3.75 (m, 4H, *ipso*Cy), 3.97 (q, 4H, J = 6.9 Hz, $OOCH_2CH_3$). ^{19}F NMR (DMSO-d6, 470.62 MHz, 298 K): δ −79.64 (apparent triplet, J = 7.3 and 10.9 Hz, 12F, CF_3), −105.80 (apparent quartet, J = 11.0 Hz, 8F, α-CF_2), −123.88 (br, 8F, β-CF_2). ^{13}C NMR (DMSO-d6, 125.77 MHz, 298 K): δ 14.4 (s, $OOCH_2CH_3$), 21.4, 25.3, 32.2, 34.2, 54.7, 62.5 (s, $OOCH_2CH_3$), 105.0–125.0 (m. $CF_2CF_2CF_3$), 146.3 (t, J = 23.9 Hz, NCN). Anal. Calcd for $C_{44}H_{54}F_{28}N_6O_4Zn_2$: C, 37.92; H, 3.91; N, 6.03%. Found: C, 37.60; H, 3.79; N, 5.80%.

Procedure for Tishchenko reaction

A 10 mL Schlenk tube was charged with the complex (25 μmol) in a drybox. The Schlenk tube was connected to a vacuum line and the aldehyde (2.5 mmol) was added. The mixture was placed in an oil-bath maintained at 80 °C and stirred vigorously. After 3 h, the tube was opened to air and aliquots of the reaction mixture were used for the NMR[79,83,90] (in $CDCl_3$) and GC/MS studies. Further, the products were isolated by column chromatography on silica gel (hexane/ether = 1 : 15 eluent).

Procedure for epoxidation of *trans*-chalcone

To a stirred solution of complex **7** (2 mmol) in toluene (5 mL), *trans*-chalcone was added (1.9 mmol) at 20 °C and the reaction mixture was stirred for 15 min and the reaction mixture was analysed by ^{1}H NMR (in $CDCl_3$) and GCMS.[60] Disappearance of the peaks corresponding to *trans*-chalcone and the appearance of the new peaks consistent with the epoxidation product, phenyl(3-phenyloxiran-2-yl)methanone was observed.

X-ray crystallographic data

A suitable crystal covered with a layer of hydrocarbon/Paratone-N oil was selected and mounted on a Cryo-loop, and immediately placed in the low temperature nitrogen stream. The X-ray intensity data for were measured at 100(2) K on a Bruker D8 Quest with a Photon 100 CMOS detector equipped with an Oxford Cryosystems 700 series cooler, a Triumph monochromator, and a Mo Ka fine-focus sealed tube (λ = 0.71073 Å). Intensity data were processed and the initial calculations for the structure determination were carried out using the SHELXTL package (version 6.14).[91] Final refinements were completed using SHELX within Olex2.[92] Hydrogen atoms were placed at calculated positions and refined riding on the corresponding carbons. All the non-hydrogen atoms were refined anisotropically. $\{[N\{(CF_3)C(2,4,6\text{-}Br_3C_6H_2)N\}_2]Zn(\mu\text{-}OEt)\}_2$ (**5**) and $\{[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]Zn(\mu\text{-}OEt)\}_2$ (**6**) crystallize with molecules of benzene in the crystal lattice. Further details are given in Table 1. The 1446335–1446338 contain the supplementary crystallographic data.

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