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Dinuclear zinc(II) pyrazolates with different degrees of ring-fluorination and their use in zinc(II) mediated olefin aziridination†‡

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Zinc complexes [{(3,5-$(CF_3)_2$Pz)ZnEt}$_2$(μ-THF)] (1), [{(3-$(CF_3$),5-(*t*-Bu)Pz)ZnEt}$_2$(μ-THF)] (2), and [{(3,5-(*i*-Pr)$_2$Pz)ZnEt}$_2$(μ-THF)] (3) adopt dinuclear structures with zinc sites bridged by a THF molecule and two pyrazolate ligands. The zinc complex 1 that features the weakest donating pyrazolate is the best catalyst among the three for the aziridination of styrene and *cis*-cyclooctene with PhI=NTs.

Fluorinated ligands play an important role in chemistry as they often allow the synthesis of metal adducts with unique structures and very useful physical properties and reactivity compared to those involving more electron rich, nonfluorinated ligand counterparts.[1] For example, [HB(3,5-$(CF_3)_2$Pz)$_3$]Cu(C_2H_4) is an air stable solid while [HB(3,5-$(CH_3)_2$Pz)$_3$]Cu(C_2H_4) decomposes quite readily in air.[2] Iron(II) complexes of fluorinated and nonfluorinated 2-pyridylimine ligands show contrasting preferences for *mer*- and *fac*-isomers leading to prismatic *vs.* tetrahedral structures and different supramolecular architectures.[3] The gold adduct {[3,5-$(CF_3)_2$Pz]Au}$_3$ is a π-acid whereas the nonfluorinated analog {[3,5-$(CH_3)_2$Pz]Au}$_3$ is a π-base.[4] Furthermore, metal complexes of fluorinated ligands have performed significantly better in palladium catalyzed aryl fluorination,[5] silver catalyzed carbene insertion to C–H and C–halogen bonds,[6] zinc catalyzed copolymerization of cyclohexene oxide and CO_2 or propylene oxide and CO_2 to name a few.[7]

Pyrazolates, which often coordinate to metal ions in an *exo*-bidentate fashion, are an especially useful and easily tunable class of ligands in coordination chemistry.[8,9] Among the many metal pyrazolate types, the zinc(II) complexes have attracted significant interest in recent years,[10,11,12–14] as some of them are known to serve as functional models of metallophosphatases and[11] drug delivery systems,[13] form metal–organic frameworks that capture toxic gases,[12] and display interesting luminescence.[9,14] However, despite the interesting and often unique outcomes of metal adducts of fluorinated ligands, zinc complexes of fluorinated pyrazolates still remain unexplored.[15] Here we report the isolation of the first such adduct supported by the highly fluorinated [3,5-$(CF_3)_2$Pz]$^-$ as well as two other zinc complexes involving sterically somewhat similar[16] pyrazolates with different degrees of fluoroalkyl ring substitution (*e.g.*, [3-$(CF_3$),5-(*t*-Bu)Pz]$^-$ and [3,5-(*i*-Pr)$_2$Pz]$^-$). We have also probed the zinc mediated aziridination chemistry of these adducts.

The zinc adduct [{(3,5-$(CF_3)_2$Pz)ZnEt}$_2$(μ-THF)] (**1**) has been synthesized by treating 3,5-$(CF_3)_2$PzH with ~1.0 equivalent of Et_2Zn *via* an ethane elimination process (Fig. 1), and obtained as a colorless, air sensitive solid in good yield. It is also possible to prepare **1** from the silver pyrazolate {[3,5-$(CF_3)_2$Pz]Ag}$_3$ and Et_2Zn, providing an alternate route if necessary.[4,17] ^{1}H NMR spectroscopic data of **1** are consistent with the pro-

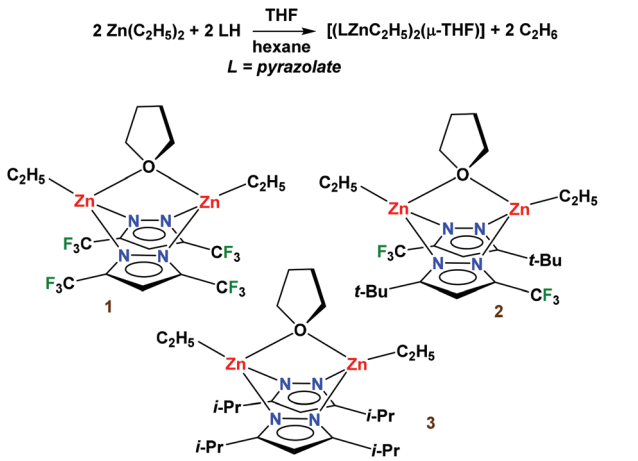

Fig. 1 Synthetic pathways to, and structures of [{(3,5-$(CF_3)_2$Pz)ZnEt}$_2$(μ-THF)] (**1**), [{(3-$(CF_3$),5-(*t*-Bu)Pz)ZnEt}$_2$(μ-THF)] (**2**), and [{(3,5-(*i*-Pr)$_2$Pz)ZnEt}$_2$(μ-THF)] (**3**).

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†This paper is dedicated to Professor Philip Power, in celebration of his 65th birthday.

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posed composition of the molecule, and indicate the presence of ethyl and pyrazolyl moieties and THF in a 2 : 2 : 1 ratio. The ^{19}F NMR spectrum of **1** displayed a singlet at δ −60.10 ppm for CF_3 fluorines which is a downfield shift from the corresponding signal of the free pyrazole, 3,5-$(CF_3)_2$PzH (δ −61.51 ppm).

The molecular structure of **1** is depicted in Fig. 2 (only one of the two chemically similar but crystallographically different molecules in the asymmetric unit are shown here). It is a dinuclear species with tetrahedral zinc sites bridged by a THF molecule and two $\eta^1:\eta^1:\mu_2$-pyrazolate ligands. Recently reported [{(3,5-$(Ph)_2$Pz)ZnEt}$_2$(μ-THF)] is the only other zinc species analogous to **1** in the literature.[15,18] Selected bond distances and angles of **1** (as well as of **2** and **3**) are given in Table 1. The Zn–N distances (av. 2.044 Å) of **1** at each zinc atom are essentially identical indicating that these ligands form a bridge in a very symmetric manner. The Zn–O bond lengths (av. 2.274 Å) are also very similar pointing to a symmetrically bridged THF moiety.

In order to examine the effects of fluoroalkyl groups on zinc pyrazolate chemistry, we have also prepared [{(3-(CF_3),5-(*t*-Bu)Pz)ZnEt}$_2$(μ-THF)] (**2**), and [{(3,5-(*i*-Pr)$_2$Pz)ZnEt}$_2$(μ-THF)] (**3**) using Et_2Zn and sterically somewhat similar but electronically different pyrazoles with one and no CF_3 groups on the pyrazolyl rings, respectively. Compounds **2** and **3** are colorless crystalline, air sensitive solids. ^{1}H and ^{19}F NMR spectroscopic data of **2** suggest the formation of one isomer out of the two possibilities (*i.e.*, both CF_3 groups pointing toward one zinc or two CF_3 groups pointing at the opposite ends of the Zn_2N_4 core as illustrated in the ESI‡). The molecular structure of [{(3-(CF_3), 5-(*t*-Bu)Pz)ZnEt}$_2$(μ-THF)] (**2**) (Fig. 3) shows that it is the isomer with each zinc atom with an identical coordination environment in which CF_3 (or *t*-butyl) groups of the two pyrazoles are pointing at the opposite directions. The Zn–N (av. 2.043 Å) and Zn–O (av. 2.255 Å) distances are similar to **1** than the corresponding parameters of **3** (Table 1). The two Zn–N distances of **2** to each zinc atom are different with the shorter distances associated with the more electron rich nitrogen atoms near *t*-butyl groups (Zn1–N1 2.0336(13), Zn2–N4 2.0291(13) Å *vs.* Zn1–N3 2.0677(13), Zn2–N2 2.0412(13) Å). The zinc(II) complex [{(3,5-(*i*-Pr)$_2$Pz)ZnEt}$_2$(μ-THF)] (**3**) features symmetrically bridged pyrazolyl moieties and THF (see the ESI‡ for the structure). The Zn–N distances of **3** (av. Zn–N 2.001 Å) are much shorter than those found with **1** indicating that shorter Zn–N distances associate with better donating nitrogen sites (as also observed with [{(3-(CF_3),5-(*t*-Bu)Pz)ZnEt}$_2$(μ-THF)] (**2**)). The Zn–O distances (Zn–O 2.3597(13) Å) of **3**, in contrast, are significantly longer than the corresponding distances of the highly fluorinated analog **1** (av. 2.255 Å) indicating probably a weaker interaction between the THF and less Lewis acidic zinc sites of the former. [{(3,5-(*i*-Pr)$_2$Pz)ZnEt}$_2$(μ-THF)] (**3**) also has a more "planar" Zn_2N_4 core and more wider inter-pyrazolyl ring angle (~133°) compared to that of **1** (*e.g.*, inter-pyrazolyl ring angle is about 107°).

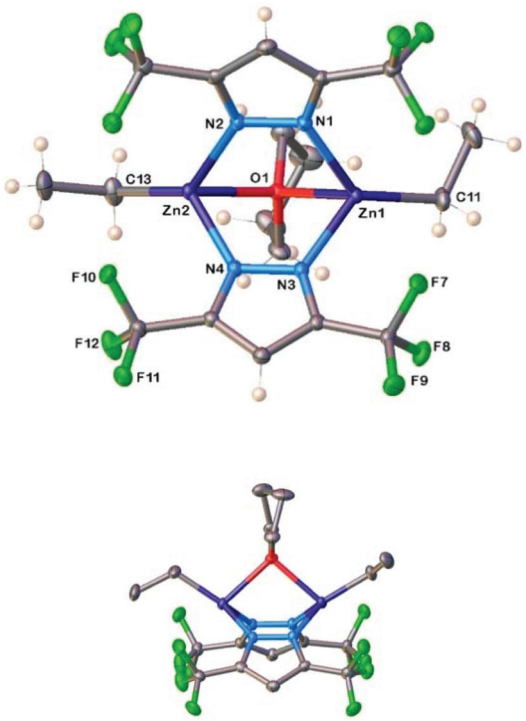


Fig. 2 X-ray crystal structure of [{(3,5-$(CF_3)_2$Pz)ZnEt}$_2$(μ-THF)] (**1**). Figure at the bottom illustrates the boat-shaped Zn_2N_4 core (H atoms are omitted for clarity).

Table 1 Selected bond distances (Å) and angles (°) for [{(3,5$(CF_3)_2$Pz) ZnEt}$_2$(μ-THF)] (**1**), [{(3-(CF_3),5-(*t*-Bu)Pz)ZnEt}$_2$(μ-THF)] (**2**) and [{(3,5-(*i*-Pr)$_2$Pz)ZnEt}$_2$(μ-THF)] (**3**). Average values are given for similar parameters with more than one value

Parameter	1	2	3
Zn–C	1.963	1.973	1.971
Zn–N	2.044	2.043	2.001
Zn–O	2.274	2.255	2.360
Zn–O–Zn	96.16	94.78	90.83
Zn⋯Zn	3.385	3.320	3.361

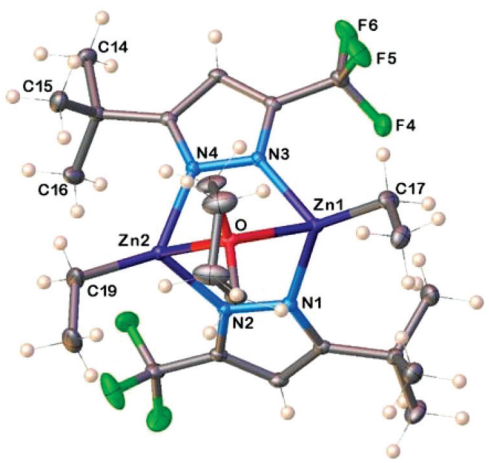
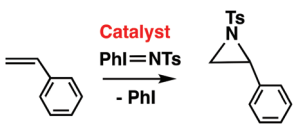


Fig. 3 X-ray crystal structure of [{(3-(CF_3),5-(*t*-Bu)Pz)ZnEt}$_2$(μ-THF)] (**2**).

In view of the tremendous interest in catalytic processes mediated by earth friendly metal ions like zinc (which is one of the cheapest and least toxic metals and ideal for applications in pharmaceutical synthesis),[19] we have investigated the ability of these zinc adducts to mediate aziridination chemistry. Aziridines are important synthetic targets and components of many biologically relevant molecules.[20–22] One of the common routes to aziridines involves the transfer of a reactive nitrene moiety (*e.g.*, from a nitrene source like *N*-tosyl phenyliodinane, PhI=NTs) to an olefin. Group 7–11 metal adducts serve as typical catalysts.[21] Interestingly, zinc complexes have not been investigated as catalysts in olefin aziridination to our knowledge. However, zinc catalyzed nitrene insertion of C–H bonds producing sulfonamides,[23] carbene addition to imines,[24] as well as a note on the use of $Zn(OTf)_2$ as one of the series of metal salts in a catalyst screening study for aziridination of methylstyrene[22] have been reported.

Our initial experiments were performed utilizing 5 mol% of the [{(3,5-$(CF_3)_2$Pz)ZnEt}$_2$(μ-THF)] catalyst, 1.0 equiv. of the nitrene source PhI=NTs, and 1.0 equiv. of the styrene in dichloromethane at 50 °C (Scheme 1 and Table 2, entry 1). We were pleased to find that under these conditions styrene gave 42% isolated yield of the olefin aziridination product, *N*-(*p*-tolylsulfonyl)-2-phenylaziridine (**4**). The yield of aziridine **4** increased upon the use of excess styrene or PhI=NTs. For example, the use of 5 mol% of the catalyst, 1.0 equiv. of the nitrene source PhI=NTs, and 3.0 equiv. of the styrene afforded the aziridination product **4** in 68% yield (Table 2, entry 4). We have probed the activity of [{(3-(CF_3),5-(*t*-Bu)Pz)ZnEt}$_2$(μ-THF)] (**2**) and [{(3,5-(*i*-Pr)$_2$Pz)ZnEt}$_2$(μ-THF)] (**3**) under the same conditions (5 mol% catalyst and 3 : 1 styrene : PhI=NTs) and found that only **2** catalyzed the aziridination but produced **4** at a relatively lower level. This indicates a notable effect of zinc Lewis acidity on this chemistry as fluorinated **1** has the most Lewis acidic zinc sites which shows the highest olefin aziridination activity, compared to the other two. The zinc complex **1** also mediates the aziridination of relatively less activated *cis*-cyclooctene (see the ESI‡).[25] However, the yield of *N*-(*p*-tolylsulfonyl)-9-azabicyclo[6.1.0]nonane (**5**) is relatively low (39% isolated yield) compared to that of **4** observed with a styrene substrate, which is not uncommon even with better-known copper systems.[25] As with styrene, **1** with more Lewis acidic zinc sites afforded the best olefin aziridination yield while **3** gave no detectable amounts of **5** under similar conditions. Copper complexes supported by weakly coordinating ligands also show better olefin aziridination activity than electron rich systems.[2,26]

In summary, we report the successful isolation of zinc adducts supported by fluorinated pyrazolates and zinc mediated olefin aziridination chemistry. Comparison of three zinc adducts of varying degrees of fluorine content shows that they all adopt basically very similar dinuclear structures. The Zn–N distances are relatively short and Zn–O distances are notably long in **3** featuring the more electron rich pyrazolate. The complex **1** with the weakest donating pyrazolate and the most Lewis acidic zinc sites shows best catalytic activity among the three adducts for the styrene or *cis*-cyclooctene aziridination with PhI=NTs. We are presently working on further improvements to these earth friendly zinc based catalysts.



Scheme 1 Aziridination of styrene using PhI=NTs.

Table 2 Results from the styrene aziridination reactions using zinc complexes [{(3,5(CF$_3$)$_2$Pz)ZnEt}$_2$(μ-THF)] (**1**), [{(3-(CF$_3$),5-(t-Bu)Pz)ZnEt}$_2$(μ-THF)] (**2**) and [{(3,5-(*i*-Pr)$_2$Pz)ZnEt}$_2$(μ-THF)] (**3**) and PhI=NTs

Entry	Catalyst (0.05 equiv.)	Styrene : PhI=NTs (equiv.)	% yield of **4** [a] (conversion)[b]
1	**1**	1 : 1	42 (61)
2	**1**	1 : 1.5	49 (68)
3	**1**	1.5 : 1	56 (70)
4	**1**	3 : 1	68 (77)
5	**2**	3 : 1	54
6	**2**	1 : 1	38
7	**3**	3 : 1	No reaction
8	**ZnBr$_2$** [c]	3 : 1	26

[a] % Isolated yield of the aziridination product **4**. [b] % conversion of styrene. [c] 0.1 equiv. of $ZnBr_2$ was used in CH_2Cl_2 : CH_3CN (1 : 1) solvent. For the catalyst **3**, TLC analysis and crude ^{1}H NMR analysis showed no signs of product **4**.

Experimental section

Synthesis of [{(3,5-(CF$_3$)$_2$Pz)ZnEt}$_2$(μ-THF)] (1)

This was synthesized by treating 3,5-$(CF_3)_2$PzH[27] (200 mg, 0.985 mmol) in THF (8 mL) with 1 M solution of Et_2Zn (1.1 mL, 1.083 mmol) in hexane. Isolated yield, 65%. ^{1}H NMR (500.16 MHz, C_6D_6, 298 K): δ 6.31 (s, 1H), 1.53 (t, J = 8.1 Hz, 3H), 0.78 (q, J = 8.0 Hz, 2H). ^{19}F NMR (470.62 MHz, C_6D_6, 298 K): δ −60.10 (s, CF_3). Compound **1** can also be synthesized from {[3,5-$(CF_3)_2$Pz]Ag}$_3$ and Et_2Zn.

Synthesis of [{(3-(CF$_3$),5-(*t*-Bu)Pz)ZnEt}$_2$(μ-THF)] (2)

This was prepared by treating 3-(CF_3),5-(*t*-Bu)PzH[27] (95 mg, 0.494 mmol) in THF (5 mL) with 1 M solution of Et_2Zn (0.54 mL, 0.544 mmol) in hexane. Isolated yield, 80%. ^{1}H NMR (500.16 MHz, C_6D_6, 298 K): δ 6.35 (s, 1H), 1.62 (t, J = 8.1 Hz, 3H), 0.73 (q, J = 8.0 Hz, 2H). ^{19}F NMR (470.62 MHz, C_6D_6, 298 K): δ −59.01 (s, CF_3).

Synthesis of [{(3,5-(*i*-Pr)$_2$Pz)ZnEt}$_2$(μ-THF)] (3). This compound was prepared by treating 3,5-(*i*-Pr)$_2$PzH (100 mg, 0.657 mmol) in THF (5 mL) with 1 M solution of Et_2Zn (0.72 mL, 0.723 mmol) in hexane. Isolated yield, 82%. ^{1}H NMR (500.16 MHz, C_6D_6, 298 K): δ 6.03 (s, 1H), 1.31 (d, J = 7.5 Hz, 12H), 3.33 (septet, 2H), 1.68 (t, J = 8.1 Hz, 3H), 0.74 (q, J = 8.0 Hz, 2H).

Crystal data for **1**, $C_{18}H_{20}F_{12}N_4OZn_2$ (M = 667.12 g mol^{-1}): triclinic, space group $P\bar{1}$ (no. 2), a = 12.5728(8) Å, b = 14.0025(8) Å, c = 14.2851(8) Å, α = 74.364(2)°, β = 84.584(2)°, γ = 88.954(2)°, V = 2411.0(2) Å^3, Z = 4, T = 101.82 K. The final R_1 was 0.0443 ($I > 2\sigma(I)$) and wR_2 was 0.1141 (all data). Crystal data for **2**, $C_{24}H_{38}F_6N_4OZn_2$ (M = 643.32 g mol^{-1}): monoclinic, space group $P2_1/c$ (no. 14), a = 10.1083(3) Å, b = 18.2839(6) Å, c = 15.3399(5) Å, β = 92.3140(10)°, V = 2832.80(16) Å^3, Z = 4, T = 100.0 K. The final R_1 was 0.0225 ($I > 2\sigma(I)$) and wR_2 was 0.0555 (all data). Crystal data for **3**, $C_{26}H_{48}N_4OZn_2$ (M = 563.42 g mol^{-1}): monoclinic, space group $C2/c$ (no. 15), a = 19.0839(7) Å, b = 8.0440(3) Å, c = 19.8329(7) Å, β = 108.2070(10)°, V = 2892.14(18) Å^3, Z = 4, T = 100.0 K. The final R_1 was 0.0259 ($I > 2\sigma(I)$) and wR_2 was 0.0694 (all data).

Procedure for the styrene aziridination reaction, Table 2, entry 4

A solution of styrene (3.0 equiv.), *N*-tosyl phenyliodinane (1.0 equiv.) and 4 Å molecular sieves (100 mg) in dry CH_2Cl_2 (6 mL) was stirred at room temperature while purging with N_2 for 2 min. Catalyst **1** (0.05 equiv.) was added, and the resulting mixture was stirred at 50 °C under N_2 for 12 h. After workup, *N*-(*p*-tolylsulfonyl)-2-phenylaziridine (**4**) was isolated as a colorless solid (54 mg, 68%).

Conflicts of interest

There are no conflicts to declare.

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