

Synthesis and structures of new binuclear zinc alkyl, aryl and aryloxo complexes

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In memoriam Professor F. Albert Cotton.

Abstract

The synthesis of a series of binuclear zinc complexes with Cl, N and O bridges is reported. The reaction of EtZnCl with B(C₆F₅)₃ in the presence of hexamethylbenzene affords the arene complex [Zn(μ-Cl)(C₆F₅)(η-C₆Me₆)₂] in which the C₆Me₆ ligand may be regarded as η³-bonded. The comproportionation of Zn[N(SiMe₃)₂]₂ with ZnBu₂ or Zn(C₆F₅)₂·toluene gave [Bu'Zn{μ-N(SiMe₃)₂}]₂ and [C₆F₅Zn{μ-N(SiMe₃)₂}]₂, respectively, with three-coordinate zinc. The reaction of ZnEt₂ with C₆F₅OH in the presence of pyridine gave [EtZn(μ-OC₆F₅)(py)]₂, while ZnMe₂ and C₆F₅OH followed by recrystallisation from THF gave [Zn(OC₆F₅)(μ-OC₆F₅)(THF)₂]₂ with five-coordinate zinc in a trigonal-bipyramidal geometry. The structures of these compounds have been determined.
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1. Introduction

Interest in organometallic zinc compounds has persisted for over 150 years. Since Frankland's synthesis of EtZnI [1], a multitude of applications have been found for such simple reagents in various fields of chemistry. For instance, alkylzinc iodides are used for Simmons–Smith cyclopropanation [2], alkylzinc bromides are used for nickel-catalyzed Negishi reactions [3] and EtZnCl generated *in situ* has been shown to be a good chain transfer agent in the polymerisation of olefins [4]. Zinc alkoxides and mixed-ligand species Zn(X)(Y), where X = bulky ligand and Y = alkyl, amide or alkoxide, are effective catalysts for the ring-opening polymerisation of lactide [5], while a number of related species as well as zinc bis(aryloxo)zinc compounds catalyze

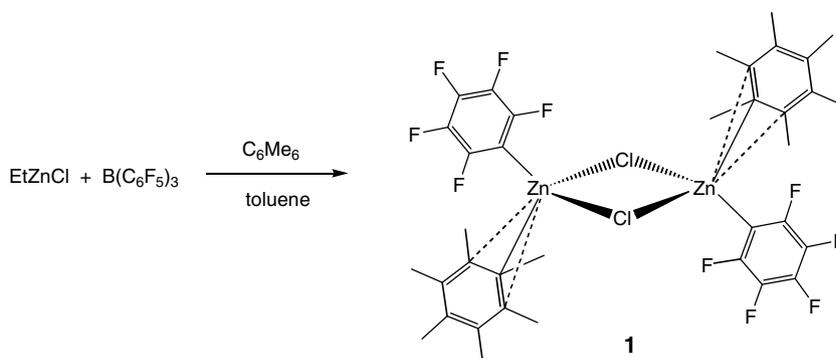
the copolymerisation of epoxides with CO₂ [6,7]. We have been interested in zinc complexes in various coordination environments as catalysts for ring-opening polymerisations of esters and ethers [8] and for isobutene polymerisations and copolymerisations [9]. In the course of these studies a number of zinc amido and aryloxo complexes were prepared as convenient starting materials, and we report here the syntheses and structural characterisation of a series of binuclear zinc alkyl, aryl and aryloxo complexes.

2. Results and discussion

The reaction of [EtZnCl]_∞ [10] with B(C₆F₅)₃ in toluene in the presence of hexamethylbenzene gave a mixture of products as a white precipitate from which some colourless crystals could be isolated by manual separation. These crystals were identified by single-crystal X-ray diffraction as the arene complex [Zn(μ-Cl)(C₆F₅)(η-C₆Me₆)₂] (1); it crystallises with one molecule of CH₂Cl₂ (Scheme 1).

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Scheme 1.

Complex **1** consists of a Zn_2Cl_2 four-membered ring with almost equal Zn–Cl distances, a hexamethyl ligand and a terminal C_6F_5 substituent (Fig. 1). The geometry around the metal centre is distorted tetrahedral, with the fourth coordination position being occupied by a hexamethylbenzene ligand which is unsymmetrically bound to the metal centre. The distance Zn–C(7) is 2.448(3) Å, whereas the distances to C(8) and C(12) are 2.714(3) and 2.767(3) Å, respectively. We have recently reported first examples of crystallographically characterised toluene complexes of zinc in which the arene ligand was rather weakly bound; $Zn(C_6F_5)_2(\eta\text{-toluene)}$ displayed a Zn–C(toluene) distance of 2.6847(15) Å, whereas the toluene ligand in $Zn(C_6F_4\text{-}2\text{-}C_6F_5)_2(\eta\text{-toluene})$ was bonded slightly more strongly, with a shortest distance to the arene of 2.524(3) Å [11,12]. By comparison, the Zn–C(arene) vector in **1** is remarkably short, indicative of a much stronger

interaction of zinc with the more electron-rich C_6Me_6 molecule than was found for toluene. We have pointed out earlier the difficulty of assigning defined hapticity to arene bonds of this kind [12]; in the case of **1** the bonding is probably best described as η^1 with a tendency towards an η^3 -interaction. The Zn–C(aryl) bond of 1.977(13) is slightly longer than that in the related three-coordinate toluene complexes $Zn(C_6F_5)_2(\eta\text{-toluene})$ (1.9436(14) Å) and $Zn(C_6F_4\text{-}2\text{-}C_6F_5)_2(\eta\text{-toluene})$ (1.951(3) Å).

Further examples of binuclear zinc complexes are readily accessible as outlined in Scheme 2.

The comproportionation of $Zn[N(SiMe_3)_2]_2$ with $ZnBu_2$ or $Zn(C_6F_5)_2 \cdot \text{toluene}$ gives the three-coordinate amido-bridged complexes $[Bu'Zn\{\mu\text{-}N(SiMe_3)_2\}]_2$ (**2**) and $[C_6F_5Zn\{\mu\text{-}N(SiMe_3)_2\}]_2$ (**3**), respectively, in good yields as colourless crystals. $[Bu'Zn\{\mu\text{-}N(SiMe_3)_2\}]_2$ is very soluble in hydrocarbons, ethers and chlorinated solvents and

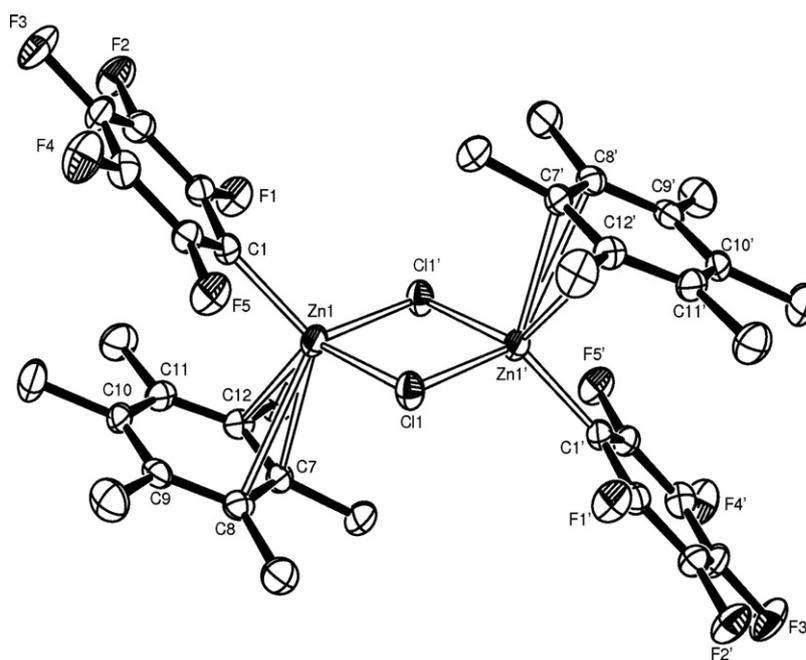
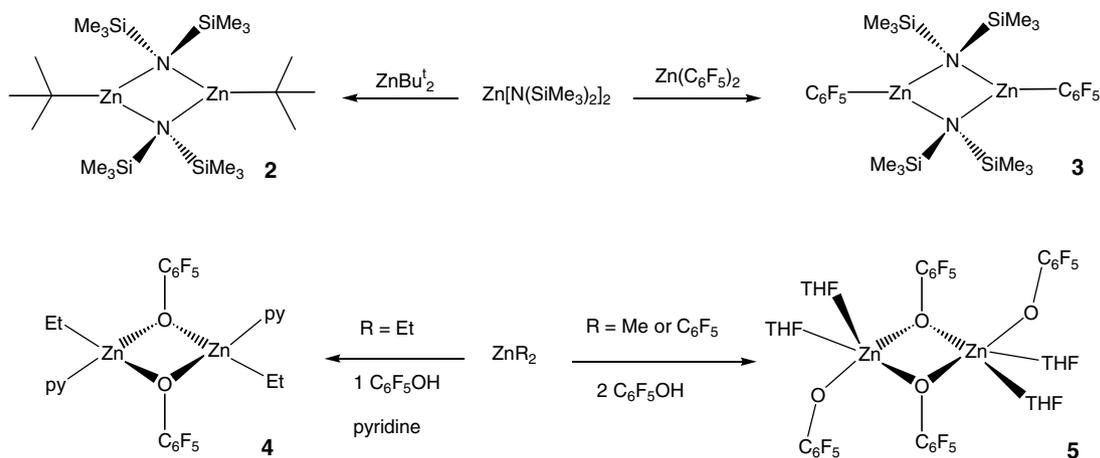


Fig. 1. Molecular structure of $[Zn(\mu\text{-}Cl)(C_6F_5)(\eta\text{-}C_6Me_6)]_2$ (**1**) showing the atomic numbering scheme and 50% probability ellipsoids; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$) with estimated standard deviations: Zn(1)–C(1) 1.977(3), Zn(1)–Cl(1) 2.3319(7), Zn(1)–Cl(1') 2.3426(8), Zn(1)–C(7) 2.448(3), Zn(1)–C(8) 2.714(3), Zn(1)–C(12) 2.767(3) Å; C(1)–Zn(1)–Cl(1) 119.60(8), C(1)–Zn(1)–Cl(1') 117.64(8), Cl(1)–Zn(1)–Cl(1') 91.97(3).



Scheme 2.

is very air-sensitive. $[\text{C}_6\text{F}_5\text{Zn}\{\mu\text{-N}(\text{SiMe}_3)_2\}]_2$ is sparingly soluble in hydrocarbons but soluble in chlorinated solvents and in ethers. It is relatively air-stable and as a solid can be briefly handled in air with no visible sign of degradation.

Interestingly, attempts to use similar comproportionation reactions to prepare the mixed-ligand zinc alkyl aryls $\text{RZn}(\text{C}_6\text{F}_5)$ from $\text{Zn}(\text{C}_6\text{F}_5)_2 \cdot \text{C}_7\text{H}_8$ and either ZnEt_2 or Zn^tBu_2 did not give the desired products; with ZnEt_2 , no reaction took place and $\text{Zn}(\text{C}_6\text{F}_5)_2 \cdot \text{C}_7\text{H}_8$ was recovered (as confirmed by ^1H and ^{19}F NMR), and with Zn^tBu_2 a small amount of intractable oily material was obtained.

The structures of **2** and **3** are shown in Figs. 2 and 3, respectively. In both cases the metal centres are three-coordinate. The Zn_2N_2 cores of both molecules are almost completely planar. The structure of **2** exhibits no obvious contacts between the zinc centres and any non-bonded atoms. Indeed, there are no short contacts with the structure using the standard definition (the sum of the van der Waals radii of the atoms). Compound **2** resembles the previously reported (low quality) structure $[\text{MeZn}\{\mu\text{-N}(\text{SiMe}_3)_2\}]_2$ [8d]. The crystals showed reactivity with air

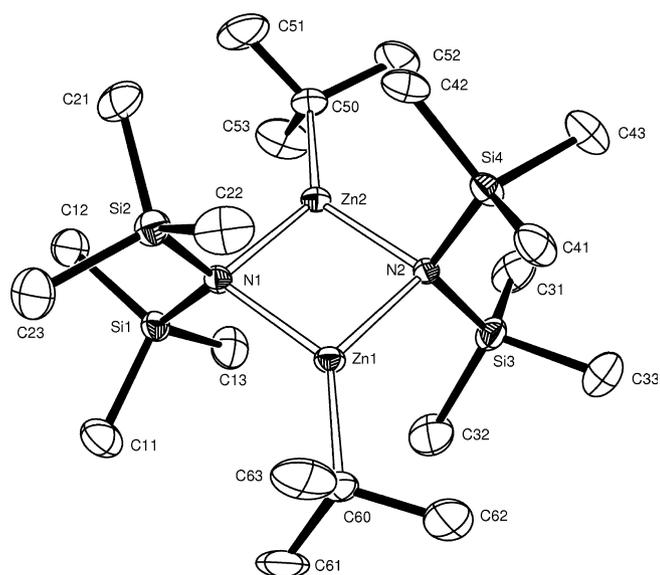


Fig. 2. Molecular structure of $[\text{Bu}^t\text{Zn}\{\mu\text{-N}(\text{SiMe}_3)_2\}]_2$ (**2**), showing 50% probability ellipsoids; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: $\text{Zn}(1)\text{-C}(60)$ 2.019(3), $\text{Zn}(2)\text{-C}(50)$ 2.021(3), $\text{Zn}(1)\text{-N}(1)$ 2.084(2), $\text{Zn}(1)\text{-N}(2)$ 2.096(2), $\text{Zn}(2)\text{-N}(1)$ 2.109(2), $\text{Zn}(2)\text{-N}(2)$ 2.086(2), $\text{Zn}(1)\cdots\text{Zn}(2)$ 2.9026(5); $\text{N}(1)\text{-Zn}(1)\text{-N}(2)$ 92.34(9), $\text{N}(1)\text{-Zn}(2)\text{-N}(2)$ 91.91(9), $\text{C}(50)\text{-Zn}(2)\text{-N}(2)$ 132.79(12), $\text{C}(50)\text{-Zn}(2)\text{-N}(1)$ 135.29(12), $\text{Zn}(1)\text{-N}(1)\text{-Zn}(2)$ 87.62(9), $\text{Zn}(1)\text{-N}(2)\text{-Zn}(2)$ 87.91(9).

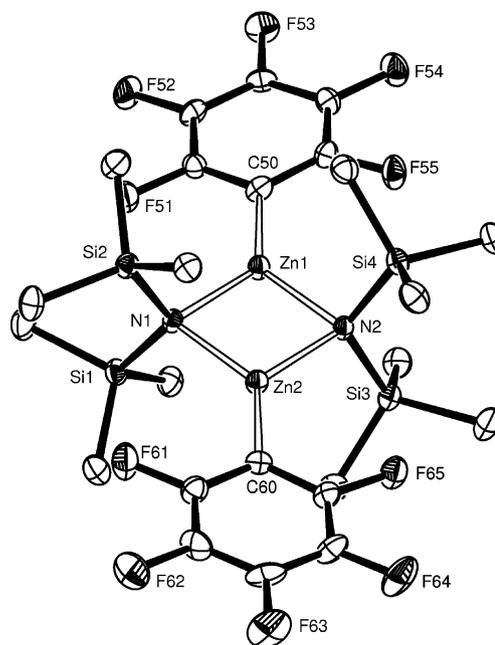


Fig. 3. Molecular structure of $[\text{C}_6\text{F}_5\text{Zn}\{\mu\text{-N}(\text{SiMe}_3)_2\}]_2$ (**3**), showing 50% probability ellipsoids; hydrogen atoms and one molecule of toluene have been omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: $\text{Zn}(1)\text{-N}(1)$ 2.048(2), $\text{Zn}(1)\text{-N}(2)$ 2.048(2), $\text{Zn}(2)\text{-N}(1)$ 2.044(2), $\text{Zn}(2)\text{-N}(2)$ 2.051(2), $\text{Zn}(1)\text{-C}(50)$ 1.983(3), $\text{Zn}(2)\text{-C}(60)$ 1.988(3); $\text{N}(1)\text{-Zn}(1)\text{-N}(2)$ 94.00(8), $\text{N}(1)\text{-Zn}(2)\text{-N}(2)$ 94.00(8), $\text{C}(50)\text{-Zn}(1)\text{-N}(1)$ 132.85(11), $\text{C}(60)\text{-Zn}(2)\text{-N}(1)$ 134.65(11), $\text{Zn}(1)\text{-N}(1)\text{-Zn}(2)$ 86.09(8), $\text{Zn}(1)\text{-N}(2)\text{-Zn}(2)$ 85.91(9).

even when under vacuum oil; this accounts for the high value of R_{int} for the data set obtained.

The Zn–N bond lengths in **3** are significantly shorter than those in **2**, a reflection of the presence of the strongly electron-withdrawing C_6F_5 ligand. On the other hand, in spite of the very different nature of the bridging atoms and the different coordination numbers, the Zn–C(aryl) distance in **3** is almost identical to that in **1**, 1.977(3) vs. 1.983(3) Å.

The protonolysis of dialkyl or diaryl zinc compounds with pentafluorophenol gives the corresponding aryloxy complexes. The reaction of diethyl zinc with pentafluorophenol in a molar ratio of 1:1 leads to the expected alkylzinc aryloxy which can be stabilised by donor ligands; e.g. ZnEt_2 and $\text{C}_6\text{F}_5\text{OH}$ in the presence of pyridine gave crystals of the complex $[\text{EtZn}(\mu\text{-OC}_6\text{F}_5)(\text{py})_2]$ (**4**), with tetrahedral metal cores. On the other hand, the reaction of 2 equivalents of $\text{C}_6\text{F}_5\text{OH}$ with either ZnMe_2 or $\text{Zn}(\text{C}_6\text{F}_5)_2 \cdot \text{toluene}$ afforded $[\text{Zn}(\text{OC}_6\text{F}_5)_2]_n$ as a white precipitate which, on recrystallisation from tetrahydrofuran, afforded colourless crystals of the THF adduct $[\text{Zn}(\text{OC}_6\text{F}_5)(\mu\text{-OC}_6\text{F}_5)(\text{THF})_2]_2$ (**5**). The structures of these compounds are shown in Figs. 4 and 5, respectively.

The two halves of the molecules in both **4** and **5** are related by an inversion centre. The geometry about the zinc atom in **4** is distorted tetrahedral. The Zn–Et bond length is closely comparable to the Zn–C distances in **1** and **3** but significantly shorter than in *tert*-butyl complex **2**, even though the latter is coordinatively less saturated. The aryl-

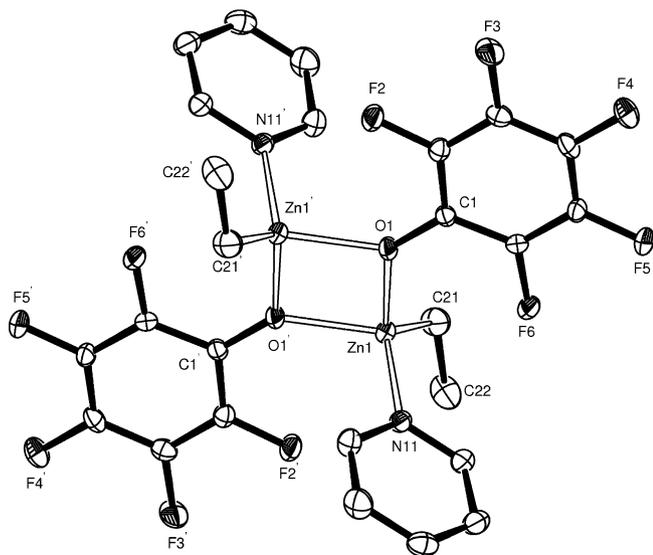


Fig. 4. Molecular structure of $[\text{EtZn}(\mu\text{-OC}_6\text{F}_5)(\text{py})_2]$ (**4**). Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. The two halves of the molecule are symmetry related by an inversion centre. Selected bond lengths (Å) and angles ($^\circ$) with estimated standard deviations: Zn(1)–C(21) 1.968(2), Zn(1)–O(1') 2.0595(12), Zn(1)–N(11) 2.0776(15), Zn(1)–O(1) 2.0858(13), C(21)–Zn(1)–O(1') 127.41(8), C(21)–Zn(1)–N(11) 123.38(8), O(1')–Zn(1)–N(11) 96.58(6), C(21)–Zn(1)–O(1) 121.56(7), O(1')–Zn(1)–O(1) 78.00(5), N(11)–Zn(1)–O(1) 98.65(6).

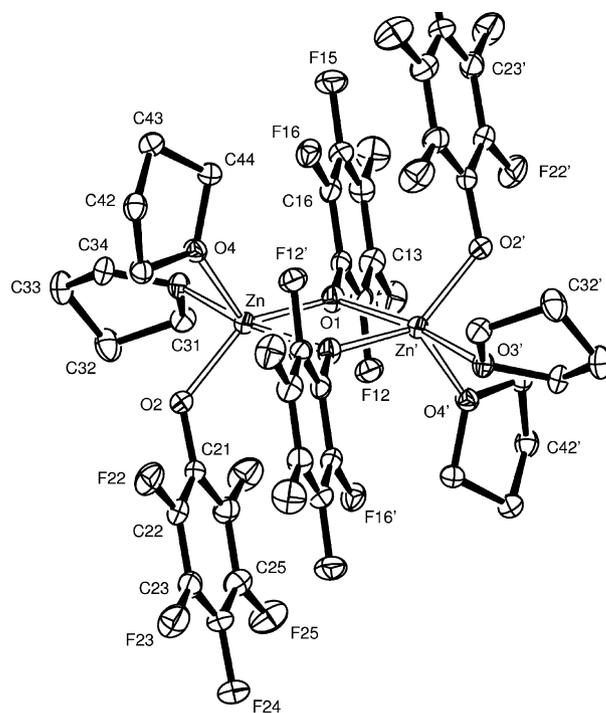


Fig. 5. Molecular structure of $[\text{Zn}(\text{OC}_6\text{F}_5)_2(\text{THF})_2]_2$ (**5**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms in the THF ligands have been omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$) with estimated standard deviations: Zn–O(1) 1.975(2), Zn–O(1') 2.136(2), Zn–O(2) 1.918(3), Zn–O(3) 2.148(2), Zn–O(4) 2.050(2); O(1)–Zn–O(2) 140.51(11), O(1)–Zn–O(3) 90.98(9), O(1)–Zn–O(4) 121.91(10), O(1)–Zn–O(1') 76.01(10), O(2)–Zn–O(3) 91.92(11), O(2)–Zn–O(4) 97.51(11), O(2)–Zn–O(1') 98.67(11), O(3)–Zn–O(1') 166.96(9), O(4)–Zn–O(3) 89.35(9), O(4)–Zn–O(1') 96.73(10), Zn–O(1)–Zn' 103.99(10), C(11)–O(1)–Zn 130.3(2), C(21)–O(2)–Zn 130.3(2), C(11)–O(1)–Zn' 125.1(2).

oxide bridges are distinctly asymmetric, with Zn–O distances of 2.0595(12) and 2.0858(13) Å, unlike the amido complexes **2** and **3** which have almost identical Zn–N bond lengths.

In contrast to the complexes discussed so far, the zinc atom in **5** is sufficiently strongly Lewis acidic to bind two THF ligands. This results in pentacoordination with a distorted trigonal-bipyramidal pattern in which one of the OC_6F_5 ligands lies in an apical site on one Zn atom and bridges to the second Zn, where it occupies an equatorial site. The aryloxy ligands form highly asymmetric bridges, with Zn–O bond distances of 1.975(2) and 2.136(2) Å. The normal to the C_6 ring of the bridging ligand is almost perpendicular to that of the central Zn_2O_2 ring plane, and the terminal OC_6F_5 ligands lie almost parallel to, and overlapping, the bridging OC_6F_5 groups. The THF ligands are well-resolved, one occupying an apical site, the other an equatorial site. The five-membered rings of both these ligands have 'half-chair' conformations in which the minimum torsion angles are 7.4(4) and 10.8(4) $^\circ$; in an envelope conformation, there is one torsion angle of 0 $^\circ$.

Compound **5** is closely related to Darendbourg's $[\text{Zn}(\text{OAr})_2(\text{THF})_2]$ (Ar = 2,6- $\text{F}_2\text{C}_6\text{H}_3$) [**7a**] which, however, contains tetrahedral zinc binding to only one THF

Table 1
Comparison of geometric parameters of binuclear zinc complexes

Compound	E–Zn–E angle (°)	Zn–E–Zn (°)	Zn···Zn distance (Å)
1, E = Cl	91.97(3)	88.03(3)	3.2481(8)
2, E = N	92.34(9), 91.91(9)	87.62(9)	2.9026(5)
3, E = N	Two at 94.00(8)	86.09(8)	2.7930(6)
4, E = O	78.00(5)	102.00(5)	3.2216(4)
5, E = O	76.01(10)	103.99(10)	3.2409(9)
[Zn(OC ₆ H ₃ F ₂) ₂ (THF)] ₂	80.07(19)	99.93(19)	3.0497(16)

ligand. By contrast, a number of other bis-THF adducts of zinc aryloxides proved to be tetrahedral monomers, Zn(OAr)₂(THF)₂ [7b]. Evidently the pentafluorophenyl substituents in **5** lead to a sufficient increase in the Lewis acidity of the metal to favour the higher coordination number. In line with this, the bond lengths to the THF and terminal aryloxide ligands in **5** are slightly longer than in [Zn(OC₆H₃F_{2-2,6})₂(THF)]₂.

In spite of the structural similarities of the compounds described here, closer inspection shows that they fall into two categories: those with E–Zn–E angles <80°, and those with >90° (where E is the bridging atom). Table 1 summarises a number of pertinent geometric features. The results show that the nature of the bridging ligand influences the structure of the Zn₂E₂ core more than the coordination number of the metal centres. The non-bonding Zn–Zn distances show significant variation, even if the bridging atoms are identical (e.g. see **2** and **3**).

3. Conclusions

Mixed-ligand zinc complexes of the type [Zn(X)(Y)]₂ are readily accessible by a variety of routes. Only highly Lewis acidic compounds like [ZnCl(C₆F₅)₂] and Zn(C₆F₅)₂ show a pronounced tendency to form stable complexes with such weak donors as arenes. Amido-bridged species are three-coordinate, whereas the more open aryloxo-bridged complexes adopt tetrahedral or trigonal-bipyramidal geometry, depending on the electron-withdrawing character of the aryl substituents, and readily bind donors like THF or pyridine. All contain planar Zn₂E₂ cores; however, these fall into two geometric categories; those with E–Zn–E angles >90° (E = Cl, N) and those with E–Zn–E ≤80° (E = O).

4. Experimental

4.1. General procedures

All manipulations were performed under argon using standard Schlenk techniques. Solvents were pre-dried, and distilled under inert atmosphere over sodium (low-sulphur toluene), sodium–benzophenone (diethyl ether, THF), sodium–potassium alloy (light petroleum, b.p.

40–60 °C) or calcium hydride (dichloromethane). NMR solvents were dried over activated 4 Å molecular sieves and degassed by several freeze-thaw cycles. NMR spectra were recorded using a Bruker Avance DPX-300 spectrometer. Chemical shifts are reported in ppm. ¹H NMR spectra (300.13 MHz) are referenced to the residual protons of the deuterated solvent used. ¹³C{¹H} NMR spectra (75.47 MHz) were referenced internally to the D-coupled ¹³C resonances of the NMR solvent. ¹⁹F (282.38 MHz) NMR spectra were referenced externally to CFCl₃. Hexamethylbenzene was purchased from Aldrich (99%) and sublimed under dynamic vacuum prior to use. Compounds EtZnCl [10], Zn[N(SiMe₃)₂]₂ [13] and Zn(C₆F₅)₂·C₆H₇ [11] were prepared according to the literature methods.

4.2. Synthesis of ZnBu₂¹

ZnBu₂¹ was prepared by modification of a method available in the literature [14]. A solution of Bu¹Li in pentane (85 mL, 1.76 M, 149.6 mmol) was added at 0 °C over a period of 1 h to a solution of ZnCl₂ (10.2 g, 74.8 mmol) in diethyl ether (200 mL). After the addition was complete, the reaction mixture was allowed to warm slowly to room temperature and stirring was then continued for another hour. The precipitate of LiCl was removed by filtration through Celite, and the solvent was removed at room temperature under vacuum to yield a yellow viscous material. ZnBu₂¹ was obtained from this oil as colourless crystals by careful sublimation under partial vacuum at room temperature, by using two traps connected in series (the first in an acetone/dry ice bath, and the second in a liquid nitrogen bath). Yield 7.1 g, 53%.

4.3. Synthesis of [Bu¹ZnN(SiMe₃)₂]₂ (**2**)

Solid Zn[N(SiMe₃)₂] (2.3 g, 5.9 mmol) was added at room temperature to a colourless solution of ZnBu₂¹ (1.0 g, 5.6 mmol) in light petroleum (40 mL), and the resulting solution was stirred overnight. The volatiles were then pumped off to yield a white powder which was dried *in vacuo* to constant weight. The target compound was obtained free of any residual Zn[N(SiMe₃)₂] by recrystallisation from a concentrated light petroleum solution (5.0 mL) stored overnight at 4 °C. X-ray quality crystals of **2** were obtained in high yield (2.8 g, 10.0 mmol, 89%) as colourless plates. The structure of the compound was determined by X-ray diffraction. ¹H NMR (CD₂Cl₂, 300.13 MHz, 25 °C): δ 1.15 (s, 9H, CMe₃), 0.09 (s, 18H, SiMe₃). ¹³C{¹H} NMR (CD₂Cl₂, 75.47 MHz, 25 °C): δ 31.2 (C(CH₃)₃), 26.3 (C(CH₃)₃), 4.8 (SiMe₃). Anal. Calc. for C₁₀H₂₇NSi₂Zn: C, 42.46; H, 9.62; N, 4.95. Found: C, 42.28; H, 9.78; N, 4.79%.

4.4. Synthesis of [(C₆F₅)ZnN(SiMe₃)₂]₂ (**3**)

Zn[N(SiMe₃)₂] (0.5 g, 1.3 mmol) was added at room temperature to a solution of Zn(C₆F₅)₂·C₆H₇ (0.6 g, 1.2 mmol)

in toluene (15 mL). Small amounts of a white precipitate formed within minutes. Stirring was continued at room temperature overnight, which resulted in the precipitation of a large amount of white solid which was filtered off, washed with light petroleum (3 × 5 mL) and dried under vacuum. Single-crystals of **3** suitable for X-ray crystallography were isolated as colourless rods by recrystallisation from a concentrated toluene solution (10 mL) kept overnight at $-26\text{ }^{\circ}\text{C}$, yield 0.8 g, (2.0 mmol, 83%). Analytical data were collected solid after drying in vacuo. ^1H NMR (CD_2Cl_2 , 300.13 MHz, $25\text{ }^{\circ}\text{C}$): δ 0.42 (s, 18H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 75.47 MHz, $25\text{ }^{\circ}\text{C}$): δ 150.7, 148.0, 143.1, 139.8, 138.7, 135.4 (all aryl- C_6F_5), 5.8 (SiMe_3). ^{19}F NMR (CD_2Cl_2 , 282.40 MHz, $25\text{ }^{\circ}\text{C}$): δ -114.2 (m, 2F, *o*-F), -155.2 (t, 1F, $J_{\text{FF}} = 19.8$ Hz, *p*-F), -162.3 (m, 2F, *m*-F). Anal. Calc. for $\text{C}_{12}\text{H}_{18}\text{F}_5\text{NSi}_2\text{Zn}$: C, 36.69; H, 4.62; N, 3.57. Found: C, 36.55; H, 4.47; N, 3.42%.

4.5. Synthesis of $[\text{EtZn}(\text{OC}_6\text{F}_5)(\text{C}_5\text{H}_5\text{N})]_2$ (**4**)

A solution of pentafluorophenol (210 mg, 1.14 mmol) in hexane (3 mL) was added to a hexane solution of diethyl zinc (1.1 mmol) containing pyridine (0.17 mL, 2.2 mmol). The mixture was stirred for 1 h at $20\text{ }^{\circ}\text{C}$. Removal of volatiles left a solid which was recrystallised from toluene at $-37\text{ }^{\circ}\text{C}$ to afford colourless crystals (0.28 g, 72%). ^1H NMR (CDCl_3 , 300.13 MHz, $25\text{ }^{\circ}\text{C}$): δ 8.66 (4H, dd, $J = 4.8$ Hz, 1.6 Hz); 7.96 (2H, dd, $J = 7.6$ Hz, 1.6 Hz); 7.55 (ddd, $J = 7.6$ Hz, 4.8 Hz, 1.3 Hz); 1.25 (6H, t, $J = 8$ Hz); 0.42 (4H, q, $J = 8$ Hz). ^{19}F NMR (CDCl_3 , 282 MHz): -163.76 (4F, br s), -167.27 (2F, t, $J = 20.6$ Hz), -177.04 (4F, br s). Anal. Calc. for $\text{C}_{26}\text{H}_{20}\text{F}_{10}\text{N}_2\text{O}_2\text{Zn}_2$: C, 43.79, H, 2.83; N, 3.93. Found: C, 43.78; H, 2.76; N, 3.92%.

4.6. Synthesis of $[\text{Zn}(\text{OC}_6\text{F}_5)_2(\text{THF})_2]_2$ (**5**)

Method A: A solution of ZnMe_2 (2.0 M in petroleum, 3.11 mL, 6.22 mmol) was added to a solution of $\text{C}_6\text{F}_5\text{OH}$ (2.29 g, 12.44 mmol) in petroleum (100 mL). A very gelatinous precipitate formed immediately.

Method B: $\text{C}_6\text{F}_5\text{OH}$ (0.45 g, 2.44 mmol) in toluene (20 mL) was added to a solution of $\text{Zn}(\text{C}_6\text{F}_5)_2 \cdot \text{toluene}$ (1.20 g, 2.44 mmol) in toluene (50 mL). At the end of addition, a white micro-crystalline precipitate began to form. ^{19}F (CD_2Cl_2): -170.06 (tt, 1F, $J = 5.2$ Hz, 21.7 Hz), -162.24 (~t, 2F, $J = 21.7$ Hz), -164.27 (~dd, 2F, 5.2 Hz, 17.5 Hz).

Recrystallisation from tetrahydrofuran at $5\text{ }^{\circ}\text{C}$ afforded colourless crystals of **5** (2.0 g, 60%) from which crystals were selected for X-ray diffraction. Anal. Calc. for $\text{C}_{40}\text{H}_{32}\text{F}_{20}\text{O}_8\text{Zn}_2$: C, 41.73; H, 2.80. Found: C, 40.85; H, 2.40%.

4.7. X-ray crystallography

The diffraction data for $[\text{ZnCl}(\text{C}_6\text{F}_5)(\text{C}_6\text{Me}_6)]_2 \cdot \text{CH}_2\text{Cl}_2$ (**1** · CH_2Cl_2), $[\text{Bu}^t\text{Zn}\{\mu\text{-N}(\text{SiMe}_3)_2\}]_2$ (**2**), and $[\text{C}_6\text{F}_5\text{Zn}\{\mu\text{-N}(\text{SiMe}_3)_2\}]_2 \cdot \text{C}_7\text{H}_8$ (**3** · C_7H_8) were collected in the cold nitrogen stream on an Oxford Diffraction Xcalibur Sapphire 3 diffractometer equipped with a Spellman DF3 molybdenum sealed-tube source operating at -50 kV , and fitted with Enhance X-ray optics. Crystals were coated in perfluorinated polyether oil, mounted on a glass fibre and fixed in the cold nitrogen stream. Data were collected at 140(2) K. Data collection and reduction was carried out using CrysAlis CCD and RED [15]. The structures were determined by direct methods using SIR92 [16] and refined on F^2 using SHELXL [17].

The data collection for $[\text{EtZn}(\mu\text{-OC}_6\text{F}_5)(\text{C}_5\text{H}_5\text{N})]_2$ (**4**) was performed on in the cold nitrogen stream of an Enraf–Nonius Kappa CCD area detector diffractometer equipped with 10 cm confocal mirrors (Mo $\text{K}\alpha$ radiation). The crystal was handled as for **1–3**. Data collection was carried out using the COLLECT package; data reduction were carried out using the software packages DENZO and SCALEPACK [17]. The structure was solved using SHELXS [17] and refined on F^2 using SHELXL [17].

For the data collection of (**5**), from a sample under oil a fragment was cut from a large crystal, mounted on a glass fibre, fixed in the cold nitrogen stream and mounted on a Rigaku R-Axis II image plate diffractometer equipped with a rotating anode X-ray source (Mo $\text{K}\alpha$ radiation) and graphite monochromator. Using 4° oscillations, 48 exposures of 30 min. each were made. Data were processed using the DENZO and SCALEPACK [18] programs. The structure was determined by the direct methods routines in the XS program [19] and refined by full-matrix least-squares methods, on F^2 in SHELXL [17]. Scattering factors for neutral atoms were taken from reference [20].

In all cases non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealised positions and their U_{iso} values were set to ride on the U_{eq} values of the parent carbon atoms. *Crystal data for 1* · CH_2Cl_2 : $[\text{ZnCl}(\text{C}_6\text{F}_5)(\text{C}_6\text{Me}_6)]_2 \cdot \text{CH}_2\text{Cl}_2$, $\text{C}_{36}\text{H}_{36}\text{Cl}_2\text{F}_{10}\text{Zn}_2 \cdot \text{CH}_2\text{Cl}_2$, colourless plate of dimensions $0.20 \times 0.10 \times 0.04$ mm, formula weight 945.21, triclinic, space group $P\bar{1}$, lattice constants $a = 9.5738(10)$ Å, $b = 9.9797(10)$ Å, $c = 10.7795(10)$ Å, $\alpha = 93.751(8)^{\circ}$, $\beta = 90.247(8)^{\circ}$, $\gamma = 113.233(10)^{\circ}$, $V = 943.86(18)$ Å³, $Z = 1$, $\mu(\text{Mo K}\alpha) = 1.631\text{ mm}^{-1}$, θ range $4.13\text{--}27.50^{\circ}$; 4305 independent reflections collected ($R_{\text{int}} = 0.0440$) of which 3159 were considered observed ($I > 2\sigma(I)$). Final R -factors were $R_1 = 0.041$ ($I > 2\sigma(I)$) $wR_2 = 0.080$ (all data).

Crystal data for 2: $[\text{Bu}^t\text{Zn}\{\mu\text{-N}(\text{SiMe}_3)_2\}]_2$, $\text{C}_{20}\text{H}_{54}\text{N}_2\text{Si}_4\text{Zn}_2$, colourless plate $0.60 \times 0.20 \times 0.10$ mm, formula weight 565.75, orthorhombic, space group $Pbca$, lattice constants $a = 16.5540(12)$ Å, $b = 21.7318(17)$ Å, $c = 17.0151(15)$ Å, $V = 6121.2(8)$ Å³, $Z = 8$; $\mu(\text{Mo K}\alpha) = 1.733\text{ mm}^{-1}$, θ range $3.56\text{--}27.74^{\circ}$; 7112 independent reflections collected ($R_{\text{int}} = 0.1572$) of which 4254 were considered observed ($I > 2\sigma(I)$). Final R -factors were $R_1 = 0.042$ ($I > 2\sigma(I)$) $wR_2 = 0.074$ (all data).

Crystal data for 3 · C_7H_8 : $[\text{C}_6\text{F}_5\text{Zn}\{\mu\text{-N}(\text{SiMe}_3)_2\}]_2 \cdot \text{C}_7\text{H}_8$, $\text{C}_{24}\text{H}_{36}\text{F}_{10}\text{N}_2\text{Si}_4\text{Zn}_2 \cdot \text{C}_7\text{H}_8$, colourless rods, crystal size

0.40 × 0.07 × 0.05 mm, formula weight 877.78, triclinic, space group $P\bar{1}$, lattice constants $a = 10.9731(13)$ Å, $b = 12.5736(7)$ Å, $c = 16.422(3)$ Å, $\alpha = 106.771(9)^\circ$, $\beta = 98.792(12)^\circ$, $\gamma = 112.112(9)^\circ$, $V = 1920.5(5)$ Å³, $Z = 2$; $\mu(\text{Mo K}\alpha) = 1.447$ mm⁻¹, θ range 3.50–27.56°; 8732 independent reflections collected ($R_{\text{int}} = 0.0559$) of which 5330 were considered observed ($I > 2\sigma(I)$). Final R -factors were $R_1 = 0.038$ ($I > 2\sigma(I)$) $wR_2 = 0.065$ (all data).

Crystal data for 4: [EtZn(μ -OC₆F₅)(C₅H₅N)]₂, C₂₆H₂₀F₁₀N₂O₂Zn₂, colourless plates, crystal size 0.16 × 0.14 × 0.05 mm, formula weight 713.2, triclinic, space group $P\bar{1}$, lattice constants $a = 7.5547(2)$ Å, $b = 9.5722(3)$ Å, $c = 9.9370(3)$ Å, $\alpha = 108.0070(10)^\circ$, $\beta = 99.419(2)^\circ$, $\gamma = 96.476(2)^\circ$, $V = 663.88(3)$ Å³, $Z = 1$; $\mu(\text{Mo K}\alpha) = 1.906$ mm⁻¹, θ range 3.2–27.5°; 3029 independent reflections collected ($R_{\text{int}} = 0.038$) of which 2825 were considered observed ($I > 2\sigma(I)$). Final R -factors were $R_1 = 0.027$ ($I > 2\sigma(I)$) $wR_2 = 0.059$ (all data).

Crystal data for 5: [Zn(OC₆F₅)₂(THF)₂]₂, C₄₀H₃₂F₂₀O₈Zn₂, colourless blocks, crystal size 0.17 × 0.17 × 0.20, formula weight = 1151.4, triclinic, space group $P\bar{1}$, lattice constants $a = 9.865(1)$ Å, $b = 10.182(2)$ Å, $c = 10.935(1)$ Å, $\alpha = 88.78(1)^\circ$, $\beta = 83.74(1)^\circ$, $\gamma = 80.21(1)^\circ$, $V = 1075.9(3)$ Å³, $Z = 1$, $\mu(\text{Mo K}\alpha) = 1.25$ mm⁻¹, θ range 1.9–25.4°, 3648 independent reflections collected ($R_{\text{int}} = 0.100$) of which 3083 were considered observed ($I > 2\sigma(I)$). Final R -factors were $R_1 = 0.056$ ($I > 2\sigma(I)$) $wR_2 = 0.140$ (all data).

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Appendix A. Supplementary material

CCDC 658162, 658163, 658164, 658160 and 658161 contain the supplementary crystallographic data for **1** · CH₂Cl₂, **2**, **3**, **4** and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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