

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

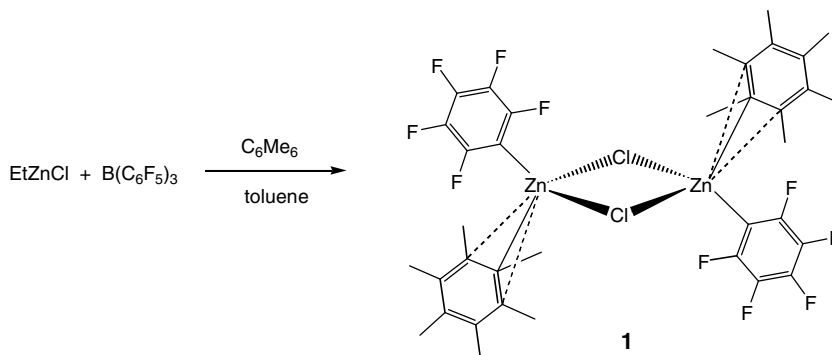
the copolymerisation of epoxides with CO₂ [6,7]. We have been interested in zinc complexes in various coordination environments as catalysts for ring-opening polymerisations of esters and ethers [8] and for isobutene polymerisations and copolymerisations [9]. In the course of these studies a number of 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

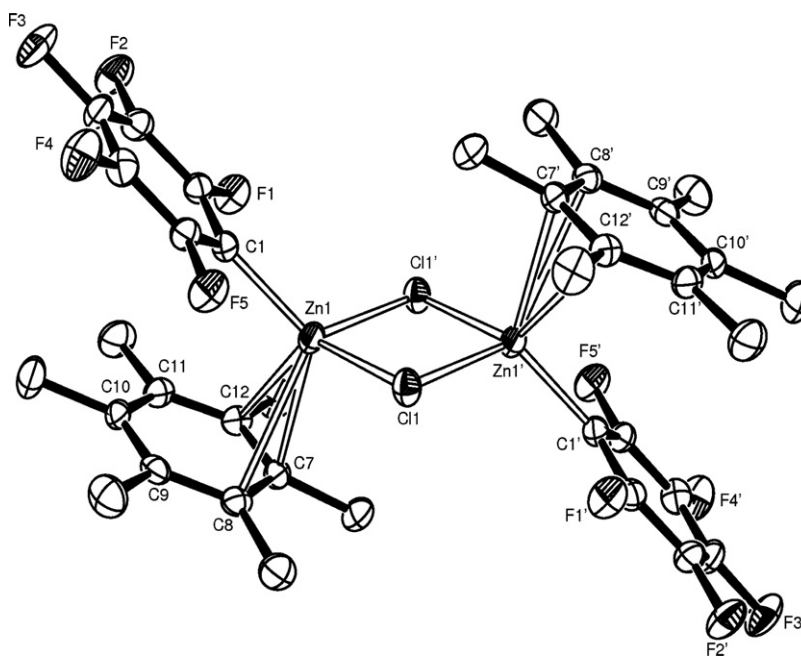


Fig. 1. Molecular structure of $[Zn(\mu\text{-}Cl)(C_6F_5)(\eta\text{-}C_6Me_6)]_2$ (**1**) showing the atomic numbering scheme and 50% probability ellipsoids; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$) with estimated standard deviations: Zn(1)–C(1) 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).

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