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Dimesitylzinc: A strictly 2-coordinate, homoleptic diarylzinc compound

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Unprecedented aryl transfer from boron to zinc generated Zn(mes)$_2$, the structure of which revealed a linear, two coordinate metal in which there is no stabilisation by inter- or intramolecular interactions.

Since the synthesis of diethylzinc in 1848 by Edward Franklin,[1] many applications of organozinc compounds in synthesis and catalysis have been documented. Detailed structural information concerning the extent of coordination and association in these species is important in understanding their physical behaviour and chemical reactivity. Gas-phase electron diffraction studies of the simple dialkyl species ZnMe$_2$, ZnEt$_2$ and Zn^{n}Pr$_2$ indicated that the structures were monomeric, with weak attraction between the zinc and the terminal methyl-substituents in the *n*-propyl derivative.[2] Solid-state X-ray structural analyses of 2-coordinate organozinc complexes were initially limited to compounds incorporating kinetically stabilising bulky groups, many related to the 'trisyl' carbanion [(Me$_3$Si)$_3$C]$^-$, including homoleptic,[3] mixed,[4] and linked ligand systems.[5] Diorganozinc compounds have also been treated with crown ethers to give structurally characterised organorotaxane species, including ZnEt$_2$(18-crown-6)[6] and ZnPh$_2$(18-crown-6).[7]

The importance of diarylzinc complexes is readily apparent from their continued use as reagents in synthesis and catalysis. For example, the homoleptic biaryl complex, ZnPh$_2$, has been used as a catalyst in the ring-opening of cyclic esters[8] and is incorporated as a component in the "diphenylzinc-additive initiator" system (ZnPh$_2$ + metallocene + MAO) for the polymerisation of olefins.[9] The molecular structure of diphenylzinc was first determined in 1990.[10] In the solid state, the ZnPh$_2$ fragments are associated into unsymmetrical dimers, [PhZn-(μ-Ph)$_2$ZnPh], that are linked by further weaker interactions into tetrameric units (Fig. 1). In contrast, the fluorinated aryl complexes Zn(Ar$_F$)$_2$ (Ar$_F$ = C$_6$F$_5$[11] and 2,4,6-(CF$_3$)$_3$C$_6$H$_2$ ≡ Fmes[12]) comprise monomeric units, in which weak intermolecular Zn ··· F interactions are present (*vide infra*).

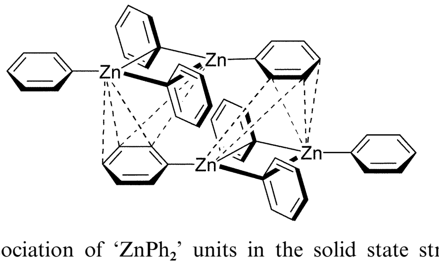
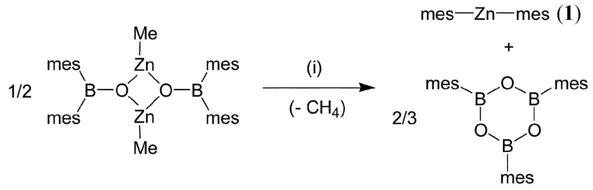


Fig. 1 Association of 'ZnPh$_2$' units in the solid state structure of diphenylzinc.

During the course of our studies into the application of the [OB(mes)$_2$]$^-$ boroxide anion as a ligand,[13] we have demonstrated that the protonolysis reaction between dimesityl borinic acid and dimethylzinc affords the zinc boroxide species, [Zn{OB(mes)$_2$}Me]$_2$.[14] At room temperature this compound is stable towards further protonolysis by a second equivalent of (mes)$_2$BOH. At elevated temperature however, a mixture of the cyclic trimer [mesBO]$_3$ and dimesitylzinc (**1**)[15] is formed, most probably according to eqn. (1).†



Reagents and conditions (i) mes$_2$BOH, toluene, 90 °C, 5 h (1)

To our knowledge, this is the first report of the transfer of an aryl group from boron to a metal centre, although related 'dearylation' of dimesitylborinic acid to afford the cyclic ester has been observed with aluminium.[16] In this case however, the boroxide species [Al{μ-OB(mes)$_2$}Me$_2$]$_2$ *catalyses* formation of [mesBO]$_3$, and mesitylene was identified as the second product of the reaction. Long needles were selected from the mixture,‡ and shown by an X-ray structure determination to be dimesitylzinc.§

The asymmetric unit of **1** consists of one mesityl group bonded to zinc, which is related to the second substituent by an inversion centre (Fig. 2). Consequently, the C(1)–Zn–C(1′) is strictly linear and the two aryl groups are coplanar with respect to each other. No such symmetry is present in the related fluorinated aryl compounds Zn(C$_6$F$_5$)$_2$ and Zn(Fmes)$_2$, resulting in Ar$_F$–Zn–Ar$_F$ angles of 172.6(2)° and 170.0(1)° respectively. The zinc–carbon bond length in **1** [1.942(2) Å] is longer than the average values for the homoleptic (C$_6$F$_5$) [1.928(4) Å] compound, and directly comparable with the Fmes derivative [1.949(3) Å].

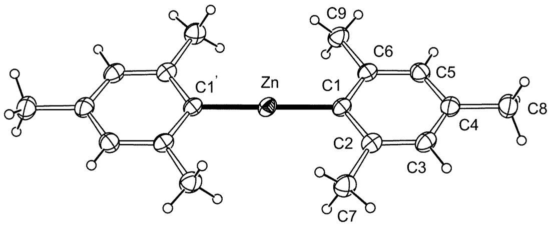


Fig. 2 Molecular structure of **1** (thermal ellipsoids 30%; ′: −*x*, −*y*, −*z*) with selected bond distances (Å) and angles (°): Zn–C(1) 1.9422(19); C(1)–Zn–C(1′) 180.

The orientation of the aryl groups in **1** is markedly different from those in the fluoroaryl derivatives. The C$_6$ rings of the Fmes compound are twisted by 67.1° and in the pentafluorophenyl analogue by 76.7°. In the former case the orientation minimises the steric congestion and electrostatic repulsion between the *ortho*-CF$_3$ groups, and in the latter compound, the rotation appears to be dictated by intermolecular stacking interactions between adjacent molecules [distance between centroids of the C$_6$F$_5$ rings = 3.503 Å and 3.563 Å]. In each of the Ar$_F$ compounds, the coordination number of the zinc is increased beyond 2 by further Zn ··· F interactions which are shorter than the sum of the van der Waals radii of the constituent atoms [2.9 Å–3.0 Å]. In the C$_6$F$_5$ derivative, the zinc is close to a *meta*-fluorine of an adjacent molecule [2.849(2) Å], and in

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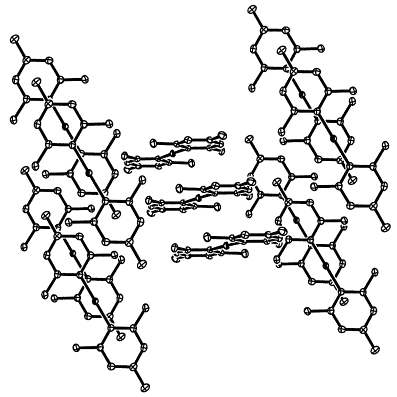

Fig. 3 View of the interpenetrating staggered layer structure in the unit cell of **1**.

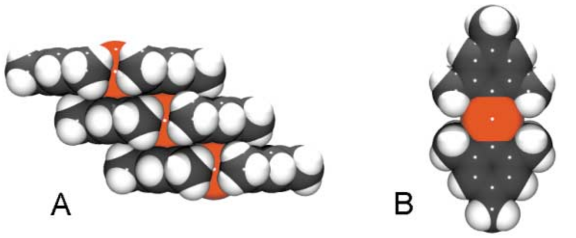

Fig. 4 Space filling diagram of (A) the layered structure and (B) *ortho*-protection of the zinc centres within **1**.

the Fmes compound, intramolecular interactions from the *ortho*-CF_3 groups are noted [2.532(6) Å–2.733(6) Å]. There are however no such secondary interactions in **1**, with the closest intramolecular distances between zinc and *ortho*-CH_3 in the range 3.00 Å–3.24 Å, considerably greater than the sum of the van der Waals radii [2.6 Å].

The planar $Zn(mes)_2$ molecules are arranged in a series of staggered layers, displaced such that the zinc atom of one molecule is located approximately equidistant between the mesityl centroids in the layer above and below (Fig. 3). The intermolecular distances between the zinc and the carbon atoms of the phenyl groups [3.725 Å–3.869 Å] are too large to be considered as denoting a bonding interaction. In the solid state therefore, the zinc atom is effectively enclosed by the layered structure, in addition to the *ortho*-methyl substituents, maintaining the strictly 2-coordinate geometry at zinc (Fig. 4). The steric bulk of the mesityl substituents is also sufficient to prevent interaction of the C_{ipso}-atom with the zinc from a neighbouring molecule, as observed in the $[ZnPh_2]_2$ dimer.

In summary, we have observed an unprecedented aryl-transfer from boron to zinc during the reaction between $(mes)_2BOH$ and $ZnMe_2$, affording $[mesBO]_3$ and $Zn(mes)_2$ (**1**). In contrast to the molecular structure of other diarylzinc complexes, the zinc centre in dimesitylzinc is strictly two-coordinate with no inter- or intramolecular stabilisation. The stability of this low-coordinate metal centre reflects the protection afforded by the mesityl substituents.

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Notes and references

† A solution of $(mes)_2BOH$ (0.500 g, 1.88 mmol) in toluene (15 mL) was added dropwise at room temperature to a stirred solution of $ZnMe_2$ (0.47 mL of 2 M solution in toluene, 0.94 mmol) which had been further diluted with an additional 10 mL toluene. The mixture was stirred overnight at room temperature and subsequently heated at reflux for 5 h. Removal of the volatiles afforded a white solid that was shown by ^1H NMR spectroscopy (C_6D_6, 298 K) to comprise $Zn(mes)_2$, δ 6.82 (Ar), 2.38 (*o*-Me), 2.23 (*p*-Me) and $[mesBO]_3$, δ 6.76 (Ar), 2.50 (*o*-Me), 2.13 (*p*-Me) in an approximate molar ratio of 1 : 1. Recrystallisation from toluene afforded colourless needles $\{Zn(mes)_2\}$ and blocks $\{[mesBO]_3\}$ that were mechanically separated.

‡ Dimesitylzinc crystallises as very long needles. When cut, the needles splinter and fragment lengthwise. It was impossible to obtain a clean short fragment and for the data collection a rather long piece, clear in the middle and frayed at the ends, was used.

§ $C_{18}H_{22}Zn$, $M = 303.73$, $T = 223(2)$ K, monoclinic, space group $P2_1/n$ (No. 14), $a = 4.9926(2)$, $b = 10.1948(3)$, $c = 15.1331(5)$ Å, $\beta = 96.618(1)°$, $U = 765.12(5)$ Å^3, $Z = 2$, $D_c = 1.32$ Mg m^{-3}, μ(Mo-Kα) = 1.59 mm^{-1}, independent reflections = 1303 ($R_{int} = 0.041$), R_1 [for 1154 reflections with $I > 2\sigma(I)$] = 0.030, wR_2 (all data) = 0.086. CCDC reference number 217302. See http://www.rsc.org/suppdata/dt/b3/b309709a/ for crystallographic data in CIF or other electronic format.

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