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Zn–Zn-Bonded Compounds that Contain Monoanionic Oxygen-Donor Ligands

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Dedicated to Professor José Barluenga on the occasion of his 70th birthday

The last years have witnessed renewed interest in the study of molecular compounds that present a metal–metal bond between atoms of Group 12 metals. For zinc, following the initial report on the structural characterisation of decamethyldizincocene, $[Zn_2(\eta^5\text{-}C_5Me_5)_2]$ (**1**),[1] a number of complexes of sterically demanding and in many cases chelating ligands have been prepared. Kinetic stabilisation of the Zn–Zn bond to prevent disproportionation to Zn^0 and Zn^{II} has been achieved by the use of different types of ligands. The initially employed bulky, substituted cyclopentadienyl units[1,2] were followed by carbon-based *m*-terphenyl groups,[3] as well as by a variety of chelating N-donor ligands,[4–6] which have also proved useful to stabilise Mg–Mg bonds.[7–9] Moreover, recent work by Schulz and co-workers has disclosed interesting reactivity of compound **1** that occurs with preservation of the Zn–Zn bond and proceeds with elimination of Cp*H ($Cp^* = C_5Me_5$).[10] Subsequently, a unique Zn_2^{2+} ion stabilised by coordination of 4-dimethylaminopyridine (dmap), $[Zn_2(dmap)_6]^{2+}$, has been isolated and structurally characterised.[10b]

Since so far Zn–Zn bonded complexes with alkoxide or aryloxide ligands (RO^-) are not known, we have decided to study the reactivity of **1** towards several alkyl and aryl alcohols. Herein, we present preliminary results on the synthesis and structural characterisation of metal–metal bonded dizinc species featuring Zn–O bonds.

As reported previously,[1,2] complex **1** reacts with Me_3COH to produce metallic zinc along with the alkoxide $[\{Zn(OtBu)_2\}_x]$. This result makes clear that bulkier RO^- groups are needed to stabilise the dizinc unit and accordingly the reactions of **1** with $Ar^{Mes}OH$ (2,6-(2,4,6-$Me_3C_6H_2$)-C_6H_3OH) and C_5Me_5OH have been investigated. Initial results were disappointing, as the low-temperature (−20°C) reaction of **1** with $Ar^{Mes}OH$ yielded an insoluble white solid that has eluded characterisation so far. Under similar conditions, C_5Me_5OH led to extensive decomposition, possibly as a result of disproportionation. We then considered providing further stabilisation to the Zn_2 unit by carrying out corresponding reactions in the presence of an N-donor ligand. Since **1** is recovered unaltered when crystallised in the presence of an excess of pyridine (despite an evident colour change to yellow that suggests weak $[Zn_2(C_5Me_5)_2]\cdots$pyridine interaction), while the more basic dmap provides the metal–metal bonded adduct $[Zn_2(C_5Me_5)_2(dmap)_2]$,[9b] it is clear that sufficiently strong an electron donor is required (pK_a values for pyridine and dmap in acetonitrile[11] are 12.53 and 17.95, respectively). With this knowledge, 4-pyrrolidinopyridine (pyr-py, $pK_a = 18.33$) and diaza-1,3-bicyclo-[5.4.0]undecane (DBU, $pK_a = 24.34$)[11] have been chosen for this study. As discussed below, these results indicate that pyr-py appears to be more appropriate than DBU for this purpose.

Low-temperature ^1H NMR spectroscopic monitoring of the reactions of **1** with $Ar^{Mes}OH$ and C_5Me_5OH (represented in general as ROH), in presence of the aforementioned N-donor L (pyr-py and DBU), reveals the consumption of both reactants, **1** and ROH, along with concomitant formation of C_5Me_5H and new zinc–zinc compounds of composition $[Zn_2(\eta^5\text{-}C_5Me_5)(OR)(L)_x]$, in which a C_5Me_5 group has been replaced by RO. For instance, treatment of **1** with $Ar^{Mes}OH$ in the presence of pyr-py leads to compound **2** as a white solid in 80% isolated yield (Scheme 1). In its ^1H NMR spectrum in C_6D_6, the methyl groups of the η^5-

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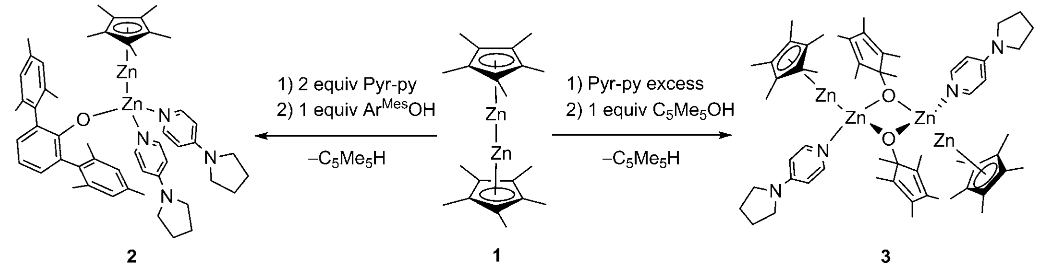

Scheme 1. Synthesis of $[Zn_2(\eta^5\text{-}C_5Me_5)(OAr^{Mes})(pyr\text{-}py)_2]$ (**2**) and $[Zn_2(\eta^5\text{-}C_5Me_5)(\mu\text{-}OC_5Me_5)(pyr\text{-}py)]_2$ (**3**).

C_5Me_5 ligand are found at 2.54 ppm (2.02 ppm in **1**) and two singlet signals at 2.27 and 2.38 ppm can be assigned to the *para-* and *ortho*-methyl substituents, respectively, of the flanking aryl rings of the aryloxide group. For the pyridinic ligand two multiplets are detected for the aromatic protons at 7.83 and 5.87 ppm. The intensity of these resonances, relative to that at 2.54 ppm due to the C_5Me_5 protons, indicates that in solution the molecules of **2** contain two pyr-py ligands. The $^{13}C\{^1H\}$ NMR spectrum of **2** discloses the expected aromatic signals for the phenyl and pyridine groups. In addition, resonances that arise from zinc-bound η^5-C_5Me_5 ligand are recorded at 11.3 (Me group) and 108.4 ppm (quaternary ring carbon nuclei).

Crystals of **2** suitable for X-ray diffraction analysis were obtained at −20 °C by slow diffusion of a solution of Ar^{Mes}OH in diethyl ether into an in situ-prepared mixture of **1** and pyr-py in toluene (see Supporting Information). The X-ray structure of **2**$\cdot C_7H_8\cdot Et_2O$ (Figure 1) confirms preservation of the Zn_2^{2+} unit, which is now stabilised by an η^5-C_5Me_5 anion coordinated to Zn1 and two pyr-py and one Ar^{Mes}O$^-$ ligands bound to Zn2. The Zn1 atom lies in an almost linear environment (Zn2-Zn1-$C_5Me_{5centroid}$ = 175.6°), whereas Zn2 resides in a distorted tetrahedral ligand distribution, similar to that found for the corresponding zinc atom in $[Zn_2(C_5Me_5)_2(dmap)_2]$.[10a] The Zn−Zn bond length in **2** of 2.3658(4) Å is significantly shorter than in the latter complex (ca. 2.42 Å), but longer than in **1** (ca. 2.31 Å).[1,2]

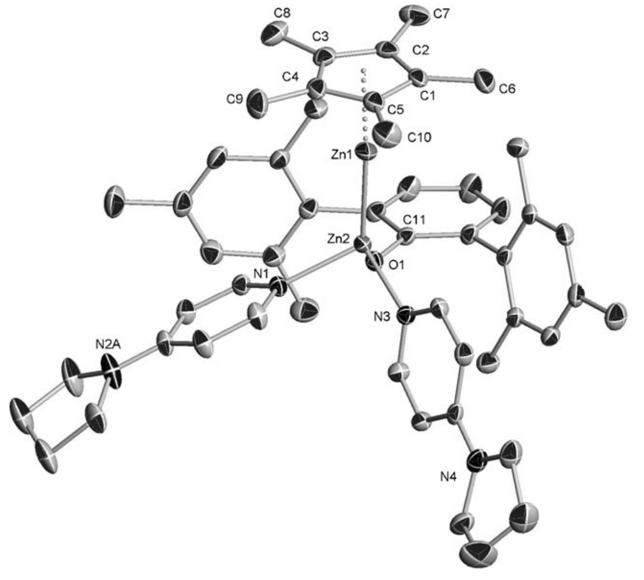

Figure 1. ORTEP representation for **2** (30 % probability displacement ellipsoids). Selected bond lengths [Å] and angles [°]: Zn1−Zn2 2.3658(4), Zn2−O1 1.940(2), Zn2−N1 2.102(2), Zn2−N3 2.089(2), Cp*$_{centroid}$−Zn1 2.002; Zn1-Zn2-Cp*$_{centroid}$ 175.6, Zn1-Zn2-N1 114.16(6), Zn1-Zn2-O1 129.53(5), Zn1-Zn2-N3 115.10(6), N1-Zn2-N3 93.63(8), O1-Zn2-N1 93.27(8), O1-Zn2-N3 103.69(8).

The above synthetic approach, whereby a protic ROH reagent is utilised to replace a C_5Me_5 group by an aryloxide ligand, may be extended to other alcohols. 2,6-Dimethyl phenol and 2,6-diisopropyl phenol are not bulky enough to stabilise the Zn_2^{2+} ion. Fast reactions ensue in the two cases at low temperature (−40 °C), yielding white solids that are only slightly soluble in solvents such as toluene and tetrahydrofuran, but insoluble in pentane or diethyl ether. Although stable as solids when stored below −20 °C, they readily decompose in solution at temperatures over −40 °C, forming black deposits of zinc metal. The instability of these compounds makes their characterisation difficult and therefore they have not been investigated any further.

At variance with these results, the reaction of **1** with C_5Me_5OH in the presence of pyr-py affords a more stable metal–metal bonded species $[\{Zn_2(\eta^5\text{-}C_5Me_5)(\mu\text{-}OC_5Me_5)(pyr\text{-}py)\}_2]$ (**3**) as a colourless, very air-sensitive solid (Scheme 1). Compound **3** is indefinitely stable as a solid at −20 °C under inert atmosphere, but decomposes slowly at room temperature, especially in solution. In contrast to **2**, complex **3** features in the solid state a dimeric arrangement consisting of two $\{(\eta^5\text{-}C_5Me_5)Zn\text{–}Zn(pyr\text{-}py)\}^+$ moieties bridged by two $C_5Me_5O^-$ ligands (Figure 2). This structural difference, when compared to **2**, may be rationalised in terms of the higher steric demands of the Ar^{Mes}O$^-$ group in relation with $C_5Me_5O^-$, which stabilises the monomeric dizinc structure. The molecules of **3** are centrosymmetric, with the four zinc atoms being coplanar with the centre of symmetry. The N atoms of the two pyr-py ligands are also almost coplanar with the zinc atoms, their deviation from the Zn_4 plane being of only 0.058 Å. As for **2**, there is a close-to-linear arrangement of the $C_5Me_{5centr.}$-Zn-Zn units (167.2°) and a distorted tetrahedral coordination environment for the alkoxide-bound zinc atoms. Bond lengths and angles around the zinc atoms are very close to corresponding values in compound **2**. In fact, the Zn−Zn bond length

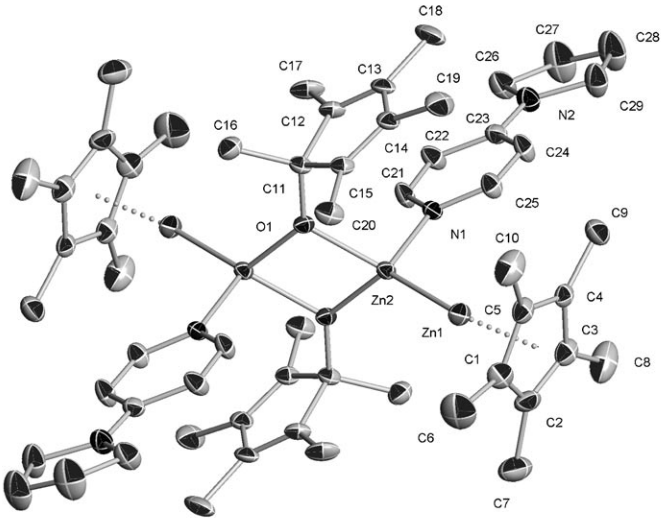

Figure 2. ORTEP representation for **3** (ellipsoids at 30 % probability). Selected bond lengths [Å] and angles [°]: Zn1–Zn2 2.366(1), Zn2–O1 2.003(5), Zn2–N1 2.124(5), Zn2–O1′ 2.004(4), $Cp^*_{centroid}$–Zn1 2.004, Zn2···Zn2′ 3.051(1); Zn1-Zn2-$Cp^*_{centroid}$ 167.2, Zn1-Zn2-N1 112.6(2), Zn1-Zn2-O1 124.9(1), Zn1-Zn2-O1′ 129.1(1), O1-Zn2-O1′ 80.8(2), O1-Zn2-N1 105.2(2), O1′-Zn2-N1 97.9(2).

of 2.366(1) Å is identical within experimental error to that in **2**.

Solution ^1H and $^{13}C\{^1H\}$ NMR data for **3** are consistent with the solid-state structure. The zinc-bonded C_5Me_5 ligand yields a singlet at 2.41 ppm for the methyl protons and $^{13}C\{^1H\}$ resonances at 11.4 and 107.8 ppm for the sp^3- and sp^2-hybridised carbon atoms, respectively. Additionally, the bridging alkoxide is responsible for ^1H NMR signals at 1.20 (α-Me), 1.67 (γ-Me) and 1.99 ppm (β-Me). Careful integration of ^1H signals due to the pyridinic protons against the η^5-C_5Me_5 resonance reveals the existence in this case of only one pyr-py ligand per C_5Me_5 ring.

Employing a similar procedure, but with the use of DBU instead of pyr-py, we have prepared the related complex $[\{Zn_2(\eta^5\text{-}C_5Me_5)(\mu\text{-}OC_5Me_5)(DBU)\}_2]$ (**4**). Although DBU is stronger a base than pyr-py (vide supra), compound **4** has poor thermal stability, probably as a consequence of the steric hindrance exerted by the molecules of DBU. As a solid, it can be stored at temperatures below −20 °C, but in solution it quickly decomposes at room temperature. Its low solubility at low temperature in common organic solvents has precluded recording its $^{13}C\{^1H\}$ NMR spectrum, but solid-state characterisation by X-ray crystallography has proved feasible (see Supporting Information). The molecular structure of this complex resembles closely that of **3**, although its Zn–Zn bonds, with a length of about 2.39 Å, are somewhat longer than in **3** and approach the value of about 2.42 Å characteristic of $[Zn_2(C_5Me_5)_2(dmap)_2]$.[10a]

In summary, we have described the isolation and structural characterisation of the first examples of zinc–zinc bonded complexes containing a Zn–O bond. Use of the bulky aryloxide ligand $Ar^{Mes}O^-$ provides access to dinuclear complexes that feature a terminal Zn-OAr^{Mes} bond, while the less sterically demanding alkoxide $C_5Me_5O^-$ yields interesting dimeric, tetranuclear structures that present two bridging alkoxide ligands joining the dizinc units. For the two types of structures the use of a strong N-containing Lewis base is needed to avoid disproportionation of the Zn_2^{2+} ion.

Experimental Section

Details on the synthesis and characterisation of the compounds reported in this paper can be found in the Supporting Information. CCDC-773521 (**2**), -773522 (**3**) and -77523 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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