Metallocenes

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Cyclopentadienyl Zincates: Synthesis and X-ray Studies of Sodium and Potassium Salts of the $[Zn(C_5H_5)_3]^-$ and $[Zn_2(C_5H_5)_5]^-$ Ions**

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Dedicated to Dr. Karl Mach on the occasion of his 70th birthday

The parent zincocene $[Zn(C_5H_5)_2]$ (**1**), was first prepared by Fischer and co-workers in 1959, by the reaction of $ZnCl_2$ and NaC_5H_5 (ca. 1:2.4 ratio), in Et_2O as the solvent, it was isolated in low yields by high-temperature sublimation of the insoluble solids under vacuum.[1] An alternative, higher-yield procedure was subsequently developed,[2] consisting in the reaction of $[Zn\{N(SiMe_3)_2\}_2]$ with freshly distilled C_5H_6, and it is routinely employed for the large-scale[3,4] synthesis of **1**. In the solid state, $[Zn(C_5H_5)_2]$ consists of infinite chains of zinc atoms bridged by cyclopentadienyl groups,[3] but the free molecules of **1** have an η^5/η^1 slip-sandwich geometry, as revealed by electron diffraction studies.[5]

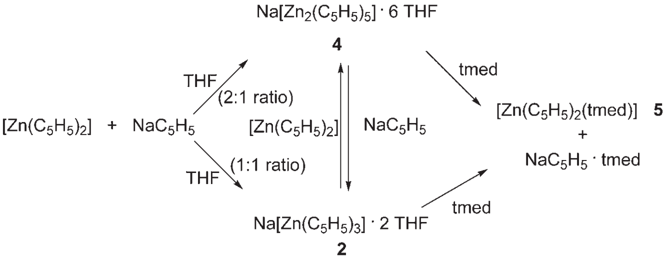
The molecules of $Zn(C_5H_5)_2$ should exhibit Lewis acid character, as found for the permethylated $[Zn(C_5Me_5)_2]$ in its reactivity toward N-heterocyclic carbenes.[6] Considering this and the prominent place that homo and heteroleptic hydrocarbyl zincates enjoy in organic and organometallic synthesis,[7–9] it is surprising that anionic adducts, for example, $[Zn(C_5H_5)_2X]^-$ (X = monoanionic Lewis base, such as H^-, alkyl, amido) have not been reported. During our studies on zincocenes[10] we have found that homoleptic zincates $[Zn(C_5H_5)_3]^-$, and dizincates $[Zn_2(C_5H_5)_5]^-$, form in good yields by minor modifications of Fischer's original procedure[1] and display interesting solid-state structures which have been determined for the alkali-metal salts $Na[Zn(C_5H_5)_3]\cdot 2\,THF$ (**2**), $K[Zn(C_5H_5)_3]$ (**3**), and $[Na(thf)_6][Zn_2(C_5H_5)_5]$ (**4**).

Compounds **2**–**4** were first obtained as unexpected products during the unsuccessful attempted synthesis of dizincocene $[Zn_2(\eta^5\text{-}C_5H_5)_2]$. Although the reduction of $[Zn(C_5H_5)_2]/ZnCl_2$ 1:1 mixtures by NaH or KH[10c] failed to give the desired metal–metal bonded dizincocene, $[Zn_2(\eta^5\text{-}C_5H_5)_2]$, it allowed the isolation of **2**–**4**, and moreover suggested that these compounds could be obtained directly from $ZnCl_2$ and NaC_5H_5 in the appropriate ratio [Eqs. (1) and (2)]. Using KC_5H_5 instead of NaC_5H_5 in the analogous reaction to Equation (1), gives only the unsolvated **3**.

$$ZnCl_2 + 3\,NaC_5H_5 \xrightarrow[THF]{20\,^\circ C,\ 18\,h,} Na[Zn(C_5H_5)_3]\cdot 2\,THF\ \mathbf{2} \qquad (1)$$

$$2\,ZnCl_2 + 5\,NaC_5H_5 \xrightarrow[THF]{20\,^\circ C,\ 18\,h,} [Na(thf)_6][Zn_2(C_5H_5)_5]\ \mathbf{4} \qquad (2)$$

The three zincate salts are colorless crystalline solids of low solubility in Et_2O, CH_2Cl_2, and hydrocarbon solvents, but readily soluble in THF. They are isolated in 60–70 % yields, and loose crystallinity under vacuum. The sodium zincates **2** and **4** can also be obtained from isolated samples of $[Zn(C_5H_5)_2]$, as shown in Scheme 1. The reactions can be reversed through the action of a Lewis base: treatment of **2** or **4** with an excess of tmed ($Me_2NCH_2CH_2NMe_2$) yields $NaC_5H_5\cdot tmed$[11] and $[Zn(C_5H_5)_2(tmed)]$ (**5**) which has been authenticated by X-ray studies to be reported elsewhere.



Scheme 1. Exchange reactions of the cyclopentadienyl zincates **2** and **4**.

The two $[Zn(C_5H_5)_3]^-$ salts, **2** and **3**, have polymeric structures in the solid state. A low-temperature X-ray crystallographic study on **2** (Figure 1)[12] shows that the structure consists of infinite nonlinear chains of alternating Zn^{2+} and Na^+ ions bridged by $C_5H_5^-$ groups. Each Zn^{2+} ion is coordinated to one terminal and to two bridging C_5H_5 rings in an almost regular planar distribution (C-Zn-C angles in the narrow range 119–122°) similar to that found in $Ga(C_5H_5)_3$.[13] The three Zn−C bonds are identical within experimental error (ca. 2.11 Å) and are longer than expected for a two-center σ Zn−C bond (about 1.95 Å[14]). This observation and

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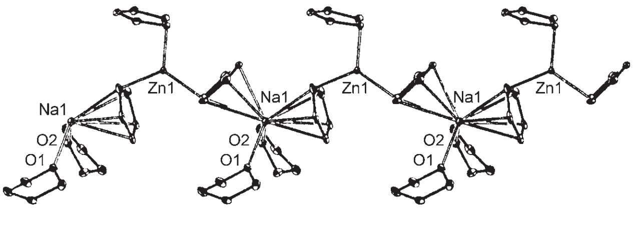

Figure 1. ORTEP diagram of **2** (thermal ellipsoids set at 50% probability) showing the coordination of the zinc and sodium ions along the *b* axis. The hydrogen atoms are omitted for clarity.

the nearly perpendicular distribution of the Zn–C bonds with respect to the C_5H_5 planes (Zn-C-ring$_{cent.}$ angles of ca. 95°) suggest $\eta^1(\pi)$ coordination of the rings.[15,16] Theoretical calculations (below) support this proposal. However, for each of the rings there is one Zn–C separation in the range 2.38–2.54 Å and while in accord with the above this may be considered as nonbonding, $\eta^2(\pi)$ coordination could also be contemplated as an approximate description of the Zn–C_5H_5 binding in this compound. The Na^+ ions are surrounded by two molecules of thf (Na–O 2.32 Å, av.) and by two C_5H_5 rings that may approximately be considered η^5, with Na–C distances of 2.74–2.93 Å.

At variance with **2**, the potassium zincate **3** has an infinite layer structure (Figure 2), in which the "zigzag" chains of ···M(C_5H_5)Zn(C_5H_5)··· units are no longer independent, but are connected with one another by means of the third C_5H_5 ring. This ring has terminal coordination in **2**, but in **3** serves as a bridge between the potassium and zinc atoms of adjacent chains. This structural difference illustrates nicely the increase in the size of the cation (for 12-coordination, the effective ionic radii of Na^+ and K^+ are 1.53 and 1.78 Å, respectively[17]).

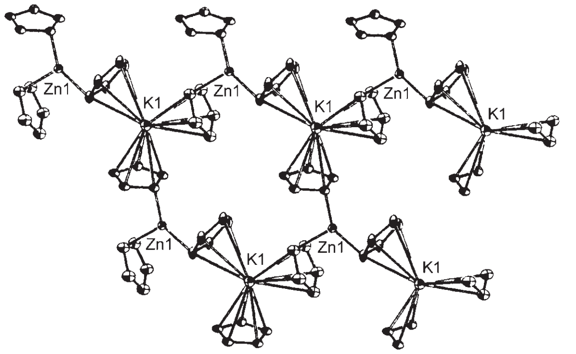

Figure 2. ORTEP diagram of **3** (thermal ellipsoids set at 50% probability). Neighboring zigzag chains of Zn···K···Zn units interconnect by bridging C_5H_5 rings across the *ab* plane. The hydrogen atoms are omitted for clarity.

The coordination of the zinc atoms in **3** is similar to that in **2** and it is characterized by Zn–C distances of 2.180(1) Å and Zn-C-ring$_{cent.}$ angles of about 95°. Once again there is one Zn–C separation close to 2.40 Å for each of the rings. The K^+ ions exhibit a coordination environment made of three η^5-C_5H_5 groups, with K–C distances in the range 3.02–3.29 Å. This is similar to the coordination found in other cyclopentadienyl potassium metalates.[18]

Whereas $M(C_5H_5)_3^-$ ions are now relatively common for main-group elements,[18b,19,20] and are also known for some d- and f-block elements,[18c,21] information on $[M_2(C_5H_5)_5]^-$ ions is sparse and appears to be limited to the $[Pb_2(C_5H_5)_5]^-$ion which contains η^5 rings.[22] The tendency of Zn^{2+} to form metallocenes of low hapticity is once again demonstrated in the solid-state structure of the $[Zn_2(C_5H_5)_5]^-$ ions of **4**, which consists of two Zn(η^1-C_5H_5)$_2$ units symmetrically bridged by a C_5H_5 group that binds to each Zn atom through a single carbon atom (Figure 3). The Zn–C distances to the terminal C_5H_5 ligands are of about 2.08 Å, while the two Zn–C bonds of the central Zn(μ-C_5H_5)Zn moiety are significantly longer, but identical within experimental error (2.17 Å, av).

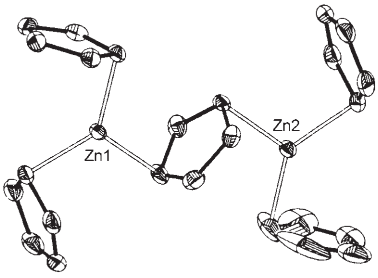

Figure 3. ORTEP diagram of the $[Zn_2(C_5H_5)_5]^-$ ion of **4** (thermal ellipsoids set at 50% probability). The hydrogen atoms are omitted for clarity. The Na^+ counterion (omitted for clarity) is octahedrally surrounded by six thf molecules, with Na–O separations between 2.33–2.39 Å.

Comparative density functional theory (DFT) calculations performed for the discrete zincate units $[Zn(C_5H_5)_3]^-$ and $[Zn_2(C_5H_5)_5]^-$ (Figure 4) yield optimized geometries that satisfactorily reproduce those found in the crystal structures. For instance, for $[Zn(C_5H_5)_3]^-$ the calculated Zn–C distances and Zn-C-ring angles are, respectively, 2.14 Å and 102°. In the computed models, the distance between the metal and the two carbon atoms adjacent to the zinc-bound carbon are longer than 2.74 Å. Hence, it is plausible that the experimentally found Zn–C distances at around 2.40 Å may result from

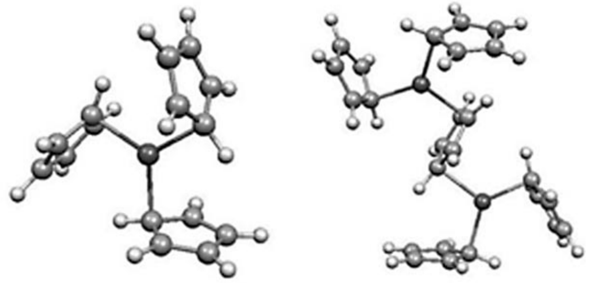

Figure 4. Optimized structures of $[Zn(C_5H_5)_3]^-$ (left) and $[Zn_2(C_5H_5)_5]^-$ (right).

crystal packing effects and that C_5H_5 binding in the $[Zn(C_5H_5)_3]^-$ ion is of the $\eta^1(\pi)$ mode or very close to it.

We have also examined the energetics of some of the reactions shown in Scheme 1. Thus, the reaction of $[Zn(C_5H_5)_2]$ with $[C_5H_5]^-$ is exothermic by almost 40 kcal mol^{-1}. Further reaction of $[Zn(C_5H_5)_3]^-$ with $[Zn(C_5H_5)_2]$ is still exothermic but only by 20 kcal mol^{-1}. However, the reaction of two molecules of $[Zn(C_5H_5)_3]^-$ to produce $[Zn_2(C_5H_5)_5]^-$ and $[C_5H_5]^-$ is endothermic by about 20 kcal mol^{-1}. These results suggest that the most stable species in solution is the $[Zn(C_5H_5)_3]^-$ ion, in good agreement with the fact that complex **2** is the only species isolated when an excess of $[C_5H_5]^-$ is used.

In summary, this work shows that cyclopentadienyl zincates are readily accessible using Fischer's original procedure for the synthesis of the neutral zincocene, $[Zn(C_5H_5)_2]$, but employing THF instead of Et_2O as the solvent.[1] Since in the original preparation $[Zn(C_5H_5)_2]$ was isolated in low yields (14%) by vacuum sublimation, the possibility that Et_2O insoluble, nonvolatile cyclopentadienyl zincates were also formed and escaped detection[1] does not appear unreasonable. In fact we have found that dizincate **4** is obtained using Fischer's procedure ($ZnCl_2$ (5 mmol), NaC_5H_5 (12 mmol), Et_2O (70 mL), reflux for 3 h) but by crystallizing the Et_2O-insoluble residue from THF instead of subjecting it to high vacuum/high-temperature sublimation. Under the same conditions but using a $ZnCl_2$:NaC_5H_5 ratio of 1:3.5, compound **2** is produced instead. Only minor amounts of $[Zn(C_5H_5)_2]$ are formed under these conditions, in accord with the original findings.[1] The $[Zn(C_5H_5)_3]^-$ structural motif adds to others already well known,[19–21] but the marked tendency of Zn^{2+} to bind to cyclopentadienyl ligands in the η^1 fashion makes this structural motif comparable only to the neutral $Ga(C_5H_5)_3$.[13] Larger M^{2+} ions, such as Ba^{2+},[20a] Sn^{2+} or Pb^{2+}[18b,20b] feature much higher overall hapticities per metal atom, of between η^9 (Sn^{2+}) to η^{20} (Ba^{2+}). In this sense, the dizincate anion of **4**, $[Zn_2(C_5H_5)_5]^-$, with a total hapticity of η^3 per zinc atom is unique since the $[Pb_2(C_5H_5)_5]^-$ ion contains terminal and bridging η^5-C_5H_5 rings.[22]

Experimental Section

All preparations and manipulations were carried out under oxygen-free argon using conventional Schlenk techniques. Solvents were rigorously dried and degassed before use. NMR spectra were recorded on Bruker AMX-300, DRX-400, and DRX-500 spectrometers. The ^1H and ^{13}C resonances of the solvent were used as the internal standard, and the chemical shifts are reported relative to TMS.

2–4: $ZnCl_2$ is added to a THF solution of MC_5H_5 in the appropriate ratio. The mixture was stirred at room temperature overnight and then centrifuged. The supernatant solution was concentrated to yield the zincate as a colorless crystalline solid. Characterization data for **4** taken as a representative example, are given below. See Supporting Information for corresponding data for **2** and **3**.

4: $ZnCl_2$ (545 mg, 4 mmol) and NaC_5H_5 (10 mL of a 1.0 M solution in THF) in THF (30 mL). Yield: 1.14 g, 30%. ^1H NMR (300 MHz, C_4D_8O, 25 °C): $\delta = 5.62$ ppm (s, 5H). $^{13}C\{^1H\}$ NMR (75 MHz, C_4D_8O, 25 °C): $\delta = 107.4$ ppm.

The geometries of the different zinc model complexes, were computed within the density functional theory at the B3LYP level,[23,24] using the 6-311+G* basis set for the Zn and C atoms and the 6-31++G** basis set for the H atoms. All the optimized geometries were characterized as local energy minima (NImag = 0) by diagonalization of the analytically computed Hessian (vibrational frequency calculations). Reaction energies were computed at the same level of theory. All the calculations were performed with the Gaussian03 package.[25] Figure were drawn using Molekel[26] Cartesian coordinates for the optimized molecules are available from the authors upon request.

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