

Zinc(II) η^1 - and η^2 -Toluene Complexes: Structure and Bonding in $\text{Zn}(\text{C}_6\text{F}_5)_2 \cdot (\text{toluene})$ and $\text{Zn}(\text{C}_6\text{F}_4\text{-2-C}_6\text{F}_5)_2 \cdot (\text{toluene})$

Antonio Guerrero,[†] Eddy Martin,[†] David L. Hughes,[†] Nikolas Kaltsoyannis,[‡] and Manfred Bochmann^{*†}

Wolfson Materials and Catalysis Centre, School of Chemical Sciences and Pharmacy, University of East Anglia, Norwich NR4 7TJ, U.K., and Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, U.K.

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Summary: The first structural characterization of toluene complexes of zinc is reported. The (perfluoroaryl)zinc compounds $\text{Zn}(\text{C}_6\text{F}_5)_2 \cdot (\text{toluene})$ and $\text{Zn}(\text{C}_6\text{F}_4\text{-2-C}_6\text{F}_5)_2 \cdot (\text{toluene})$ show toluene in η^2 and η^1 coordination modes, respectively. On the other hand, charge distribution calculations, Mulliken overlap population analysis, and bonding energy data suggest that the interactions between the Zn and the toluene ring are rather similar in both cases.

The propensity of zinc to form π complexes with anionic organometallic moieties is, of course, well-known.^{1–7} Probably the best example of this type of complex is bis(cyclopentadienyl)zinc, with its polymeric $[\text{Zn}(\eta^2\text{-C}_5\text{H}_5)_2]_\infty$ structure.⁵ Similar asymmetric η^2 interactions have also been documented for zinc allyls⁷ and, most recently, for zinc divinyl compounds, where η^2 coordination leads to the formation of coordination polymers in the solid state.⁸ In contrast, although the Zn^{2+} ion and many zinc(II) compounds are known for their Lewis acid behavior and readily bind polar molecules, well-characterized complexes of zinc coordinated to neutral $\text{C}=\text{C}$ π systems are remarkable for their scarcity. In early pioneering studies on the system $\text{Zn}(\text{SbF}_6)_2/\text{arene}$ in liquid SO_2 , Damude and Dean⁹ isolated solid 1:1 products of the composition $\text{Zn}(\text{SbF}_6)_2 \cdot (\text{arene})$ for electron-rich arenes (C_6HMe_5 and C_6Me_6); solution spectroscopic studies showed labile zinc–arene interactions which, in analogy to the known copper(I)¹⁰ and silver(I)¹¹ systems, were interpreted as localized bonding of the arene to the metal cation. Weak

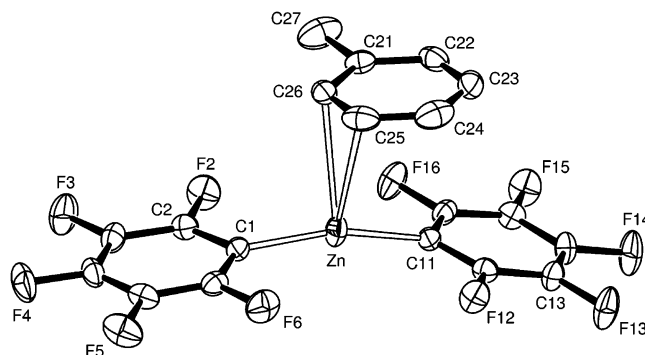


Figure 1. View of a molecule of $\text{Zn}(\text{C}_6\text{F}_5)_2 \cdot (\text{toluene})$ (**1**), indicating the atom-numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (deg): $\text{Zn}-\text{C}(1) = 1.9436(14)$, $\text{Zn}-\text{C}(11) = 1.9419(15)$, $\text{Zn}-\text{C}(25) = 2.784(2)$, $\text{Zn}-\text{C}(26) = 2.6847(15)$; $\text{C}(11)-\text{Zn}-\text{C}(1) = 162.35(6)$.

intramolecular interactions between Zn(II) centers and aryl substituents have been structurally identified, as in Power's thiolato complexes $\text{Zn}(\text{SC}_6\text{H}_3\text{-2,6-Ar}_2)_2$ ($\text{Ar} = 2,4,6\text{-R}_3\text{C}_6\text{H}_2$, $\text{R} = \text{Me}$, Pr^i)¹² or in core-modified porphyrin complexes.¹³ Adducts between zinc porphyrinato complexes and toluene are also known, although in this case this is a π -stacking interaction with the planar porphyrinato system, rather than specific toluene coordination to the metal center.¹⁴

A few years ago we described the synthesis of $\text{Zn}(\text{C}_6\text{F}_5)_2 \cdot (\text{toluene})$, where toluene could be readily displaced by more electron rich arenes such as hexamethylbenzene.¹⁵ At the time, no crystals suitable for X-ray diffraction could be obtained, and the nature of the zinc–arene bonding, if any, could therefore not be ascertained. We now report the first structurally confirmed examples of isolable zinc complexes with η^1 - and η^2 -coordinated toluene.

As reported earlier, the reaction of $\text{B}(\text{C}_6\text{F}_5)_3$ with ZnMe_2 in toluene provides a convenient route to $\text{Zn}(\text{C}_6\text{F}_5)_2 \cdot (\text{toluene})$ (**1**) in high yield. The compound is usually isolated as colorless needles.¹⁵ Leaving a toluene solution of **1** standing in an NMR tube has now provided colorless block-shaped crystals of the compound that proved suitable for crystallographic examination.¹⁶ The structure (Figure 1) shows a slightly angled $\text{Zn}(\text{C}_6\text{F}_5)_2$ molecule (angle $\text{C}(11)-\text{Zn}-\text{C}(1)$ $162.35(6)^\circ$). The two C_6F_5 ligands are oriented almost perpendicular to the $\text{C}(1)-\text{Zn}-\text{C}(11)$ plane. The third coordination site on zinc is occupied by a toluene molecule that is asymmetrically bonded to the metal center, with the bond distance to the C atom in an ortho position being shorter than that to meta C. Although the distances $\text{Zn}-\text{C}(25) = 2.784(2)$ Å and $\text{Zn}-\text{C}(26) = 2.6847(15)$ Å are 0.74

[†] University of East Anglia.

[‡] University College London.

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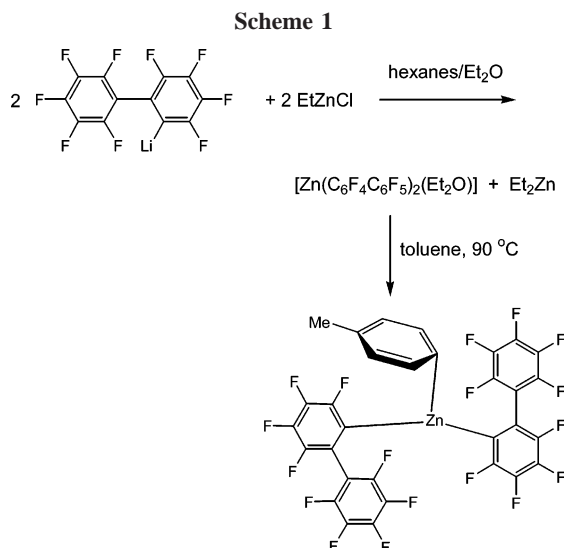
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and 0.84 Å longer, respectively, than the average Zn–C₆F₅ bonds, they are shorter than the sum of the zinc and carbon covalent radii and are clearly within bonding range.

Attempts were made to prepare a bulkier analogue of Zn(C₆F₅)₂, bis(2-perfluorobiphenyl)zinc. Initial reactions between LiC₆F₄-2-C₆F₅¹⁷ and ZnCl₂ gave only intractable products. However, the reaction of EtZnCl with LiC₆F₄-2-C₆F₅, generated in situ from 2-bromononafluorobiphenyl and ⁿBuLi in a light petroleum/diethyl ether mixture, gave a clean white solid. We assume that the initial product, EtZn(C₆F₄-2-C₆F₅), disproportionates into Et₂Zn and an ether adduct of Zn(C₆F₄-2-C₆F₅)₂, which was not isolated. Residual diethyl ether was removed by heating this solid with toluene at 90 °C while passing a nitrogen stream over the solution (Scheme 1).¹⁸

Cooling to –26 °C afforded colorless crystals of Zn(C₆F₄-2-C₆F₅)₂·(toluene) (**2**) (Figure 2).¹⁹ The Zn–aryl bonds are comparable to those in **1**. However, the toluene ligand in **2** is bonded to zinc via the para C atom, not via the ortho and meta C atoms, and the Zn–C(toluene) bond length in **2** is significantly shorter than in **1**, 2.524(3) Å. In agreement with a stronger metal–toluene interaction, the C(1a)–Zn–C(1b) angle is more acute, 153.26(11)°.

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(16) Crystal data for **1**: C₁₉H₈F₁₀Zn, fw = 491.6, monoclinic, space group P2₁/n (No. 14), a = 14.7241(12) Å, b = 6.7216(4) Å, c = 18.7794(15) Å, β = 108.099(7)°, V = 1766.6(2) Å³. Z = 4, D_c = 1.848 g cm⁻³, F(000) = 968, T = 140(2) K, μ(Mo Kα) = 14.9 cm⁻¹. The total number of reflections recorded, to θ_{max} = 27.5°, was 22 516, of which 4043 were unique (R_{int} = 0.034); 3289 were “observed” with I > 2σ_i. The structure was determined by direct methods routines. wR2 = 0.064 and R1 = 0.033 for all 4043 reflections weighted with w = [σ²(F_o²) + (0.0381P)² + 0.073P]⁻¹ and P = (F_o² + 2F_c²)/3; for the “observed” data only, R1 = 0.023.

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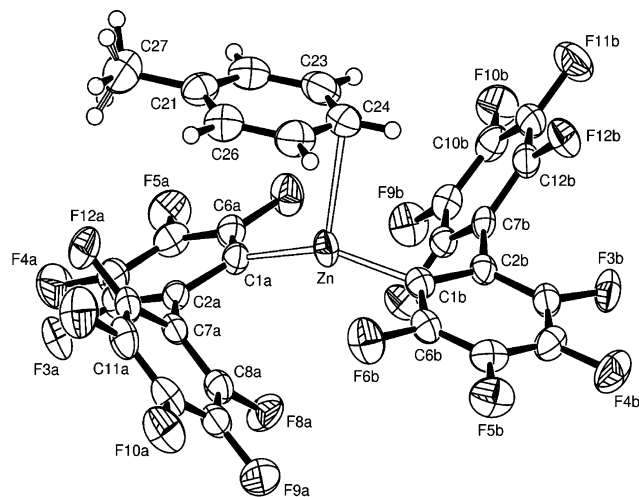


Figure 2. View of a molecule of Zn(C₆F₄-2-C₆F₅)₂·(toluene) (**2**), indicating the atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (deg): Zn–C(1a) = 1.951(3), Zn–C(1b) = 1.949(3), Zn–C(24) = 2.524(3); C(1b)–Zn–C(1a) = 153.26(11), C(1a)–Zn–C(24) = 112.96(11), C(1b)–Zn–C(24) = 93.55(11).

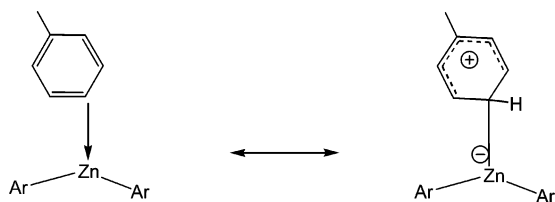
The bonding of toluene to zinc in these systems was explored in more detail using molecular orbital calculations.²⁰ In particular, we wished to establish whether in the η¹-toluene complex there was a significant contribution from a zwitterionic resonance structure (Scheme 2), akin to the formation of the well-known silylium ion [Et₃Si·(toluene)]⁺, which contains σ-bonded

(18) To a stirred solution containing 2-bromononafluorobiphenyl (2.26 g, 18.3 mmol) in light petroleum/diethyl ether (1/1, 250 mL) at –78 °C was added dropwise ⁿBuLi in hexanes (11.4 mL, 18.3 mmol). The initially colorless solution turned green and was stirred for a further 3 h. Solid EtZnCl (2.38 g, 18.3 mmol) was added at –78 °C, and the solution was slowly allowed to reach room temperature. A white solid formed, and the mixture was stirred for a further 30 min before the solvent was evaporated at reduced pressure. Toluene (250 mL) was added, and the mixture was heated to 90 °C while a stream of nitrogen was passed over the solution. After 2 h the hot solution was filtered, the solvent volume was reduced to 40 mL, and the solution was allowed to crystallize at –26 °C to afford the title compound as colorless plates (4.46 g, 62%). Anal. Calcd for C₃₁H₈F₁₈Zn: C, 47.26; H, 1.02. Found: C, 46.85; H, 0.76. ¹H NMR (C₆D₆): δ 7.02 (5H, C₆H₅), 2.10 (3H, CH₃). ¹⁹F NMR (C₆D₆): δ –119.03 (dd, 2F, J_{FF} = 26.5 Hz, J_{FF} = 11.8 Hz, *o*-F), –134.98 (m, 2F), –141.59 (dt, 4F, J_{FF} = 22.3 Hz, J_{FF} = 9.0 Hz, *o*'-F), –151.63 (t, 2F, J_{FF} = 21.7 Hz), –151.99 (ddd, 2F, J_{FF} = 23.4 Hz, J_{FF} = 20.0 Hz, J_{FF} = 5.6 Hz), –152.78 (td, 2F, J_{FF} = 20.0 Hz, J_{FF} = 3.1 Hz), –160.07 (tdd, 4F, J_{FF} = 22.3 Hz, J_{FF} = 7.0 Hz, J_{FF} = 2.0 Hz, *m*-F). ¹³C NMR (C₆D₆): δ 148.37, 148.05, 145.89, 140.07, 139.44, 137.86, 129.28 (C₆H₅), 128.51 (C₆H₅), 125.64 (C₆H₅), 114.93, 21.37 (CH₃).

(19) Crystal data for **2**: C₃₁H₈F₁₈Zn, fw = 787.7, triclinic, space group P1̄ (No. 2), a = 10.5464(12) Å, b = 11.5033(12) Å, c = 12.2157(16) Å, α = 78.844(10)°, β = 77.811(10)°, γ = 74.448(10)°, V = 1380.7(3) Å³. Z = 2, D_c = 1.895 g cm⁻³, F(000) = 772, T = 180(1) K, μ(Mo Kα) = 10.4 cm⁻¹. The total number of reflections recorded, to θ_{max} = 25°, was 15 221, of which 4846 were unique (R_{int} = 0.064); 3623 were “observed” with I > 2σ_i. wR2 = 0.091 and R1 = 0.055 for all 4846 reflections weighted with w = [σ²(F_o²) + (0.0536P)² + 0.073P]⁻¹ and P = (F_o² + 2F_c²)/3; for the “observed” data only, R1 = 0.037.

(20) Single-point calculations on **1** and **2** were performed at their crystallographic geometries using the Gaussian 03 (revision D.01; Frisch, M. J. et al. Gaussian Inc., Wallingford, CT, 2004) and Amsterdam Density Functional codes (version 2005.01b: te Velde, G.; Bickelhaupt, F. M.; van Gisbergen, S. J. A.; Fonseca Guerra, C.; Baerends, E. J.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931). The PBE GGA exchange and correlation functionals were employed. For the Gaussian 03 calculations, the 6-311++G** basis set was employed, and the SCF convergence criterion was set to “tight”. For the single-point ADF calculations, the all-electron TZP basis sets were used. Geometry optimizations were also performed using the ADF code. The frozen core approximation was employed (Zn(2p), C(1s), F(1s)), and the energy gradient convergence criterion was set to 0.001 au/Å. All other parameters were employed at their default values.

Scheme 2



toluene.^{21,22} A single-point calculation on **2** gives a natural charge for the zinc atom of 1.37. The natural charges on the C atoms of the toluene ring, starting from C(Me), are 0.00 (ipso), -0.19 (ortho), -0.22 (meta), and -0.33 (para), with the last being the C atom bonded to the Zn. There is therefore no evidence for a Wheland-type structure, which would imply positive charge delocalization over the toluene ring. For the η^2 complex, the Zn has a charge of 1.35. As one goes around the toluene ring, starting from C(Me), the charges are -0.02 , -0.20 , -0.19 , -0.21 , -0.25 , and -0.28 , where the last two are the C atoms bonded to the Zn. Hirshfeld charge analysis, while producing absolute values different from those of the natural approach, also finds little difference between the charges on corresponding atoms in **1** and **2**. Hence, the calculations suggest that, despite the differences in Zn–C distances and bonding modes apparent from the solid-state structure, the charge distributions in compounds **1** and **2** are quite similar.

Mulliken overlap populations may be considered to be the number of electrons covalently bonding between two atoms. The Zn–C(C₆F₅) overlap populations in **2** are 0.74 and 0.77 e, not unsurprising for single bonds. In contrast, the overlap populations between the Zn atom and the C of the toluene rings in **1** and **2** are much smaller; 0.12 e in **2** and 0.06 and 0.08 e in **1**. This suggests not only that there is comparatively little Zn–toluene covalent bonding in both **1** and **2** but also that, as noted in the charge analyses, the interactions between the Zn and the toluene rings are rather similar in both cases.

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(22) The related aluminum compound Al(C₆F₅)₃(η^1 -toluene) is better represented by a π coordination model: Hair, G. S.; Cowley, A. H.; Jones, R. A.; McBurnett, B. G.; Voigt, A. *J. Am. Chem. Soc.* **1999**, *121*, 4922.

The zinc–toluene bonds are weak: the interaction energy between the toluene ring and the Zn-containing fragment in **1** is 25.4 kJ mol⁻¹. The value for the η^1 complex **2** is rather similar, 27.9 kJ mol⁻¹. To probe this further, geometry optimizations of **1** and **2** in the gas phase were performed, using the ADF code and starting from the crystallographic coordinates. Both calculations readily converged to geometries that were very similar to the starting structures, except for the Zn–C(toluenes) distances, which were ca. 0.2 Å longer than in the crystal structures. A further geometry optimization of **1**, in which the toluene was initially placed in an η^1 arrangement, also readily converged to a structure in which the η^1 coordination was retained. This structure is only 1 kJ mol⁻¹ less stable than the η^2 coordinated optimized **1**, indicating that the potential surface for toluene coordination is very flat.

π stacking between toluene and C₆F₅, as suggested by a reviewer, is unlikely to be significant in these structures. In **1** the best planes between C₆F₅ and toluene form an angle of 16.2°, with a centroid–centroid distance of 4.05 Å. There are no near-parallel oriented arene moieties in **2**. To further probe the possible contribution of toluene–C₆F₅ attractive forces, the energies of interaction between the toluene ring and the closest perfluorophenyl ring in both systems were calculated, yielding 2.7 kJ mol⁻¹ for **1** and 3.1 kJ mol⁻¹ for **2**. We believe these values are too small to be structure directing.

The overall conclusion, therefore, is that, while the crystallographic data point to a distinct difference between the Zn–toluene bonding in **1** and **2**, the computed electronic structures indicate relatively weak zinc–arene π bonding and emphasize the similarity of arene bonding in both cases.

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Supporting Information Available: Tables giving crystallographic data and structure refinement details for **1** and **2**; crystal data are also given as CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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