

Abstract No. wu301

High-Resolution Electron Density Analysis of a Proposed Agostic Interaction in $\text{Zr}(2,4\text{-C}_7\text{H}_{11})(\text{C}_3\text{H}_7\text{N-C}_8\text{H}_{12}\text{-C}_5\text{H}_5)$

G. Wu, S. Pillet (SUNY, Buffalo), R. Ernst (U. Utah), and P. Coppens (SUNY, Buffalo)

Beamline(s): X3A1

Introduction: Electron density analysis with highly accurate low temperature data allows unusually detailed analysis of the bonding in complex molecules. A short $\text{Zr}\cdots\text{H}$ (2.46 Å) distance in the title compound (Figure 1) suggest the possibility of an agostic interaction between the H atom and the empty d-orbitals of the early transition metal Zr atom, in analogy with similar interactions confirmed in Ti complexes.

Methods and Materials: Data were collected on a $0.11\times 0.10\times 0.06$ mm³ crystal at about 16 K, using a He gas flow system installed at the X3A1 beamline. Topological analysis [1] of the total electron density, as obtained from an aspherical atom (multipole) refinement is used to yield net charges integrated over the atomic basins and to obtain insight into the nature of the bonding between the atoms.

Results: Figure 2 shows the gradient trajectories of the electron density in the relevant Zr-N-C-H plane. The Zr-N, N-C and C16-H bonds exhibit topological features characteristics of direct bonding: a bond path, a bond critical point (CP) and the sharing of an interatomic surface. No bond CP or bond path is located along the $\text{Zr}\cdots\text{H}$ vector, indicating the absence of direct interactions between these atoms. The atomic charge of the H atom, obtained by numerical integration over its atomic basin is positive, in contradiction with the proposed negative hydrogen charge for an agostic interaction involving empty d-orbitals. Only one bond CP is found between the metal center and the pentadiene ligand, in the Zr-C direction. Two Zr-C bond CPs link the Zr with the butadiene moiety. The strongest interaction occurs with the nitrogen atom, with an electron density at the bond CP of 0.85 eÅ⁻³. The Laplacian of the electron density at the coordination bond CPs is positive, as usually observed for metal-ligand bonds.

Conclusions: Notwithstanding the short metal-hydrogen distance, an agostic interaction is absent in this complex. The strongest Zr-ligand bond occurs with the nitrogen atom of the $\text{CN}(\text{CH}_3)_2$ group.

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References:

[1]. A. Volkov, C. Gatti, Yu. Abramov, and P. Coppens, "Evaluation of Net Atomic Charges and Atomic and Molecular Electrostatic Moments Through Topological Analysis of the Experimental Charge Density, *Acta Crystallogr. A*, **56**, 252, 2000.

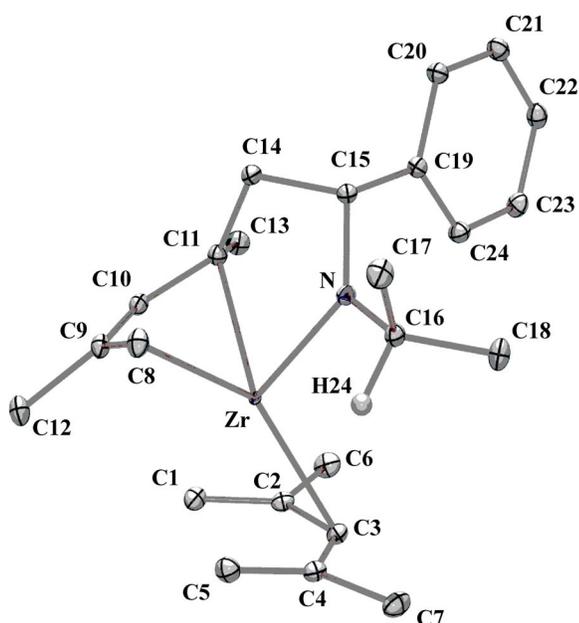


Figure 1. Structure of the title compound.

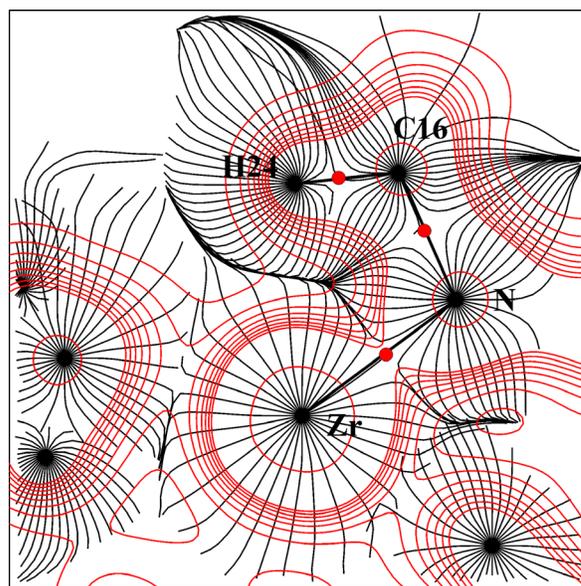


Figure 2. Gradient trajectories (black lines) and total electron density (red lines) in the Zr-N-H plane. Bond CPs are depicted as squares. A contour interval of 0.1 eÅ⁻³ is used for the electron