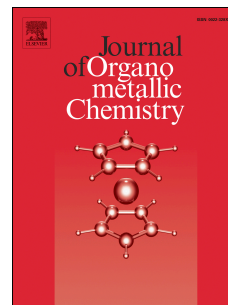


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The $(C_5Me_5)_2(Sr,Sm)$ connection

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Dispersion and Distortion in Heavy Group 2 and Lanthanide Decamethylmetallocenes: the $(C_5Me_5)_2(Sr,Sm)$ Connection¹

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Highlights

- 10
- Computational investigation of “bent” (non-linear) metallocenes, $(C_5R_5)_2Sr$ and $(C_5H_5)_2Sm$.
 - Use of “dispersion-free” density functional APF and dispersion-corrected version APF-D.
 - $(C_5H_5)_2Sm$ bends without assistance of dispersion interactions.
 - DFT indicates that both electronic (orbital) and dispersion effects affect the bending of $(C_5Me_5)_2Sr$

Abstract

15 Identification of the source(s) of the counterintuitive bending (non-linearity) in heavy group 2 (Ca–Ba) dihalides and metallocenes has long been in dispute, a difficulty compounded by the low values of energy involved (ca. $\lesssim 2$ kcal mol⁻¹). Analogous issues exist with compounds of the divalent lanthanides Sm(II), Eu(II), and Yb(II), despite the substantially different electronic structures of the metals involved. The assertion that the bent structure of $(C_5Me_5)_2Sr$, for
20 example, can be attributed exclusively to the operation of attractive dispersion forces between the ring methyl groups has been argued on the basis of molecular mechanics calculations, and more recently with the aid of DFT studies that employed dispersion-corrected density functionals (Organometallics, 32(5) (2012), 1265). In contrast, covalent interactions have been identified as the primary source of bending in the similarly distorted $(C_5Me_5)_2Sm$. The case of bent
25 $(C_5Me_5)_2Sr$ has been reinvestigated with the use of larger basis sets for strontium, and with the employment of the “dispersion-free” APF density functional. We find that given flexible enough

¹ Dedicated to Prof. William J. Evans, a mentor and friend, on the occasion of his 70th birthday.

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