

The Dichotomy of Dimetalloenes: Coaxial versus Perpendicular Dimetal Units in Sandwich Compounds

Yaoming Xie, Henry F. Schaefer III, and R. Bruce King*

Department of Chemistry and Center for Computational Chemistry, University of Georgia, Athens, Georgia 30602

Received December 1, 2004; E-mail: rbking@sunchem.chem.uga.edu

One of the most exciting recent developments in organometallic chemistry has been the discovery of the first dimetalloene more than 50 years after the original discovery of ferrocene. Thus, decamethylzincocene, $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Zn}_2$ (Figure 1), was unexpectedly obtained from the reaction of $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Zn}$ with Et_2Zn .¹ This is the first example of an “extended metallocene” in which a pair of metal atoms is sandwiched between two cyclopentadienyl rings such that the metal–metal bond is collinear with the C_5 axes of the cyclopentadienyl (Cp) rings. This Communication describes our initial attempts using density functional methods to explore the possible range of such dimetalloenes. Our computations suggest that two distinctly different structure types for dimetalloenes are possible, namely, the coaxial structure found experimentally for $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Zn}_2$ and a second type of structure, predicted for dicuprocenes, Cp_2Cu_2 , in which the metal–metal bond axis is perpendicular to rather than collinear with the C_5 axes of the Cp rings.

Two selected density functional theory (DFT) methods, including the B3LYP2 and BP86³ methods, were used. The DZP basis sets for the C and H atoms are Huzinaga–Dunning’s contracted double- ζ sets⁴ plus polarization functions with orbital exponents $\alpha_d(\text{C}) = 0.75$ and $\alpha_p(\text{H}) = 0.85$. For the transition metals (Ni, Cu, and Zn), the loosely contracted DZP basis sets are the Wachters’ primitive sets⁵ augmented by two sets of p functions and one set of d functions, contracted following Hood et al.⁶ The basis set used in this work for C may be designated as (9s5p1d/4s2p1d), that for H as (4s1p/2s1p), and those for Ni, Cu, and Zn as (14s11p6d/10s8p3d). All of the computations were carried out with the Gaussian 94 program.⁷

The DFT computations on the unsubstituted $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zn}_2$ indicate the coaxial D_{5h} structure (Figure 1) expected from the reported¹ experimental results with the Zn–Zn bond collinear with the C_5 axis. The computed Zn–Zn distance is 2.336 (B3LYP) or 2.315 Å (BP86), which is close to the experimental value¹ of 2.305 Å for the permethylated derivative.

In their paper, Resa, Carmona, Gutierrez-Puebla, and Monge¹ devoted a sizable part of their manuscript to describing their crystallographic and spectroscopic work demonstrating that hydride ligands are not present in the structure of Cp_2^*Zn_2 . This was done to avoid a repeat of the now discredited claim of an unsupported cobalt–cobalt bond in Cp_2^*Co_2 . Therefore, we have computationally considered the $\text{CpZn}(\mu\text{-H})_2\text{ZnCp}$ structure using the analogous levels of theory. We predict that $\text{CpZn}(\mu\text{-H})_2\text{ZnCp}$ is not stable but dissociates to $\text{CpZnH} + \text{HZnCp}$.

Specifically the C_{2v} symmetry structure with Zn–H distances of 2.272 and 2.279 Å is predicted to lie 60 kcal/mol above $\text{CpZnH} + \text{HZnCp}$. This $\text{CpZn}(\mu\text{-H})_2\text{ZnCp}$ structure is a transition state with one imaginary vibrational frequency, 1688 i cm^{-1} . In this structure, the Zn–Zn distance is 4.482 Å, much longer than the 2.336 Å found for CpZnZnCp . The energetics of the reaction

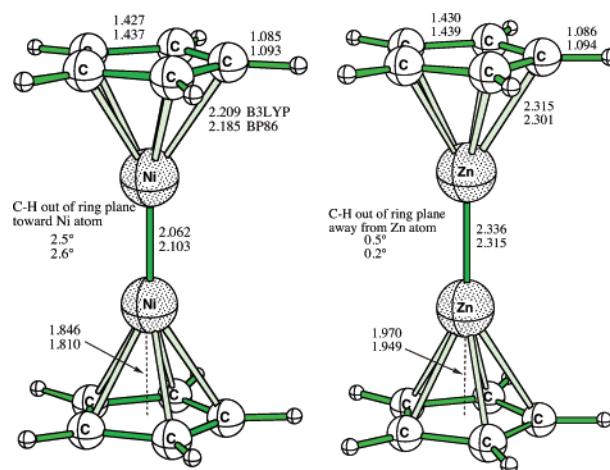
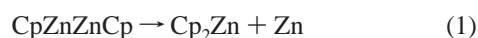


Figure 1. Coaxial closed-shell singlet structures for $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}_2$ (M = Zn and Ni). All bond distances are in angstroms.

are also of interest since in several reactions described by Carmona et al.,¹ disproportionation occurs to yield a Zn(II)-containing species and elemental zinc. We predict here that reaction 1 is endothermic by 20 kcal/mol, further supporting the stability of CpZnZnCp .

Similar computations were performed on the corresponding Cp_2M_2 derivatives for the metals immediately preceding zinc in the Periodic Table. A closely related coaxial D_{5h} structure (Figure 1) was found for dinickelocene, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}_2$, except for the shorter metal–metal distance of 2.062 Å in accord with the $\text{Ni}\equiv\text{Ni}$ triple bond required to give the Ni atoms the favored 18-electron noble gas configuration. Note that dinickelocene is diamagnetic in contrast to the long-known nickelocene, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}$, which is paramagnetic, corresponding to two unpaired electrons.

The structures reported in Figure 1 are eclipsed, that is, they display D_{5h} symmetry. The staggered D_{5d} structures were also optimized and have the same energy to within 0.01 kcal/mol. In essence, for both CpZnZnCp and CpNiNiCp , there is free rotation about the metal–metal bond. Natural bond orbital (NBO) analyses have been carried out for all structures. For CpZnZnCp , the single bond displays hybridization $\text{sp}^{0.03\text{d}0.01}$, indicating a nearly pure s character. For CpNiNiZp , the σ bond is similar to the above, while the two π bonds are almost pure d_{xz} and d_{yz} orbitals. A qualitative molecular orbital diagram for the frontier orbitals of the dimetalloene structures of CpNiNiCp , CpCuCuCp (triplet electronic ground state), and CpZnZnCp is shown in Figure 2.

The axial dimetalloene structure for dicuprocene, $(\eta^5\text{-C}_5\text{H}_5)_2\text{-Cu}_2$, would require a $\text{Cu}=\text{Cu}$ double bond to give each metal atom the favored 18-electron configuration. This triplet dicuprocene (D_{5h} symmetry) with a $\text{Cu}=\text{Cu}$ double bond similar to that in dioxygen or $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\mu\text{-CO})_3$ is shown in Figure 3.

Efforts to optimize the structure of singlet dicuprocene gave a totally different structure from that of its Zn_2 analogue. In the new

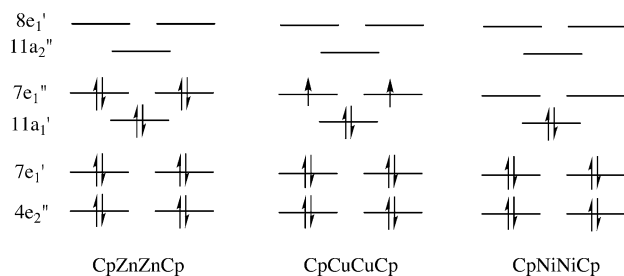


Figure 2. Molecular orbital diagram for the dimetalocene structures.

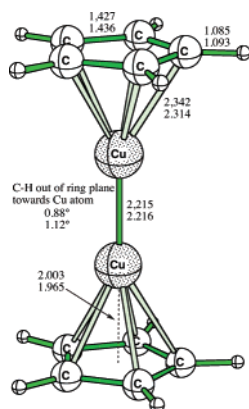


Figure 3. Coaxial structure for the triplet state of $(C_5H_5)_2Cu_2$.

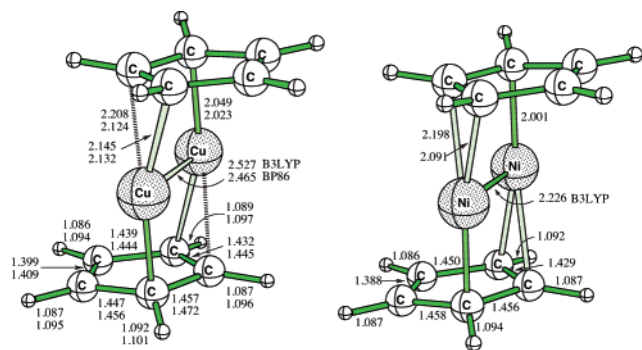


Figure 4. Perpendicular structures for singlet $(C_5H_5)_2Cu_2$ and $(C_5H_5)_2Ni_2$.

structural type, the metal–metal bond is perpendicular to the C_5 axis of the Cp rings, leading to overall C_i symmetry (Figure 4).

This perpendicular Cp_2Cu_2 structure (Figure 4) is predicted to lie 75 kcal/mol (B3LYP) below the coaxial structure seen in Figure 3.

In the perpendicular structure for dicuprocene (Figure 4), each copper atom is bonded to a portion of both Cp rings, in contrast to the axial structures for dizincocene and dinickelocene in which each metal atom is bonded to only one of the Cp rings. In the dicuprocene structure (Figure 4), each Cu atom is η^2 -bonded to an olefin portion of one Cp ring and η^3 -bonded to an allyl group of the other Cp ring using the $\{s, p_x, p_y\}$ orbital set. This bonding scheme gives each Cu atom a 16-electron configuration similar to the planar coordination of other late transition metals. The Cu–Cu distance of 2.523 (B3LYP) or 2.467 Å (BP86) suggests a metal–metal interaction similar to that found in the stacking of other square planar

complexes. Furthermore, a related $[(C_6H_6)_2Pd_2]^{2+}$ unit with the Pd–Pd axis perpendicular to the C_6 axes of the benzene rings and an experimental Pd–Pd distance of 2.57 Å is found in the benzene-palladium complexes $(C_6H_6)_2Pd_2(AlCl_4)_2$ and $(C_6H_6)_2Pd_2(Al_2Cl_7)_2$, first reported in 1970.⁸ Having found this fascinating $(C_5H_5)_2Cu_2$ structure, we were curious to know if the analogous nickel and zinc perpendicular structures might be stable. For $(C_5H_5)_2Zn_2$, this perpendicular structure is not a stationary point, but collapses to the D_{5d} structure. However, for $(C_5H_5)_2Ni_2$, the perpendicular structure (Figure 4) lies 52 kcal/mol (B3LYP) below the coaxial structure seen in Figure 1.

The successful synthesis of a dizincocene derivative¹ makes dicuprocenes and dinickelocenes interesting and reasonable synthetic objectives. Furthermore, the ability to alter the steric and electronic properties of Cp rings by suitable choices of substituents provides considerable flexibility in synthetic strategies. Dicuprocenes should be obtainable using suitably chosen copper(I) halide derivatives and cyclopentadienides of suitably chosen electropositive metals. A trimer of dinickelocene, namely, the octahedral cluster $(\eta^5-C_5H_5)_6Ni_6$, was first isolated from the reduction of nickelocene with sodium naphthalenide⁹ and has subsequently been isolated from various reactions of nickelocene with lithium and magnesium alkyls containing β -hydrogen atoms.¹⁰ Similar reactions using nickelocene derivatives with bulky substituents to inhibit trimerization of Cp_2Ni_2 to Cp_6Ni_6 might provide successful synthetic routes to dinickelocenes. Dinickelocenes might also be accessible by decarbonylation (thermal or photochemical) of suitably chosen $Cp_2Ni_2(\mu-CO)_2$ derivatives.

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Note Added in Proof. The beryllium, magnesium, and calcium dimetalocenes have been examined in *Chem. Phys. Lett.* **2005**, *402*, 414.

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