

Note

# A topological isomer of ferrocene: Theoretical approach for transition metal complexes with conjugated all *trans* cyclodecapentaene

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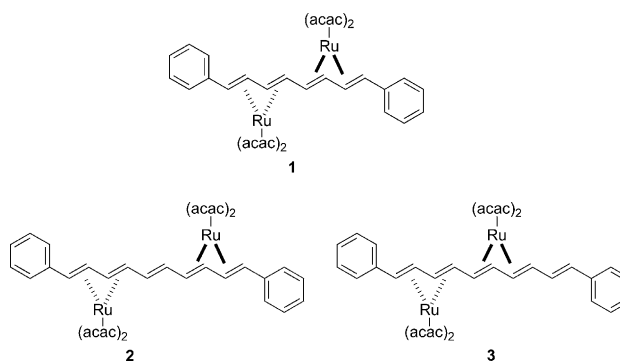
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## Abstract

We demonstrate the ability of all-*trans* DPEN as a suitable ligand for transition metals by DFT computation [B3LYP/6-311+G(2d,p) and BP86 level]. The iron complex Fe(DPEN) is a unique topological isomer of ferrocene.  
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Since the discovery of ferrocene in early 1950s, organometallic chemistry of transition metals has been developed extensively in terms of the fundamental bonding, physical properties, and attracting applications as catalysts as well as source for materials. We have been interested in this field and, particularly, *s-trans* diene complexes of transition metals last two decades [1–3]. The scope of mononuclear transition metal that coordinate in *s-trans* fashion to diene unit expanded soon after the first discovery of Group 4 metals [4–9] to Groups 5, 6, and 8 metals [10]. Considering the importance of orbital conjugation in the diene complexes, we investigated the complexation of extended conjugated system, i.e.,  $\alpha,\omega$ -diphenylpolyenes, to prepare dinuclear tetraene and pentaene complexes 1–3 bearing Ru(acac)<sub>2</sub> [11,12]. Kurosawa et al. reported several linear palladium clusters supported by two polyene ligands [13].

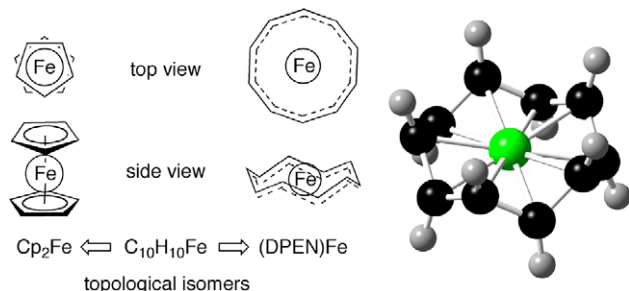


According to crystallographic data, the *s-trans* diene ligand in these *s-trans* complexes is highly distorted from the planarity, two terminal carbon–carbon bonds being deformed about 30°. We anticipate that it may be possible to create cyclic polyene coordinating systems, the smallest one being all-*trans* cyclodeca-1,3,5,7,9-pentaene (DPEN). Although the linear diphenyl pentaene ligand is accessible and complexes 2 and 3 were able to be prepared, our preparative efforts have been hampered by the instability of the DPEN ligand. Thus, by using

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DFT computation [B3LYP/6-311+G(2d,p) and BP86 level], we examined the capability of all-*trans* DPEN as a ligand for transition metals. We found that iron(0) and some other transition metals coordinated by DPEN are stable molecules and unique topological isomers of the corresponding metallocene complexes.



Since the cyclic pentaene provides aromatic 10 electrons [14] the metal should have equal or less than eight electrons. At first, we calculated Fe(0)–DPEN complex and the results by B3LYP/6-311+G(2d,p) level computation are shown in Fig. 1. The shape and levels of some orbital interactions including HOMO and LUMO of the iron complex indicate the strong bonding interaction between Fe(0) and DPEN through the aromatic  $p\pi$ -electrons of DPEN.

We calculated some other DPEN complexes with 18 electron configuration in BP86 level. Two complexes with axial  $\pi$ -acidic coligands,  $(\text{DPEN})\text{Ti}(\text{CO})_2$  and  $[(\text{DPEN})\text{V}(\text{CO})_2]^+$ , together with a dichloro chromium complex were selected and their computational results are summarized in Tables 1 and 2. In the course of this studies, all calculations were performed for a singlet

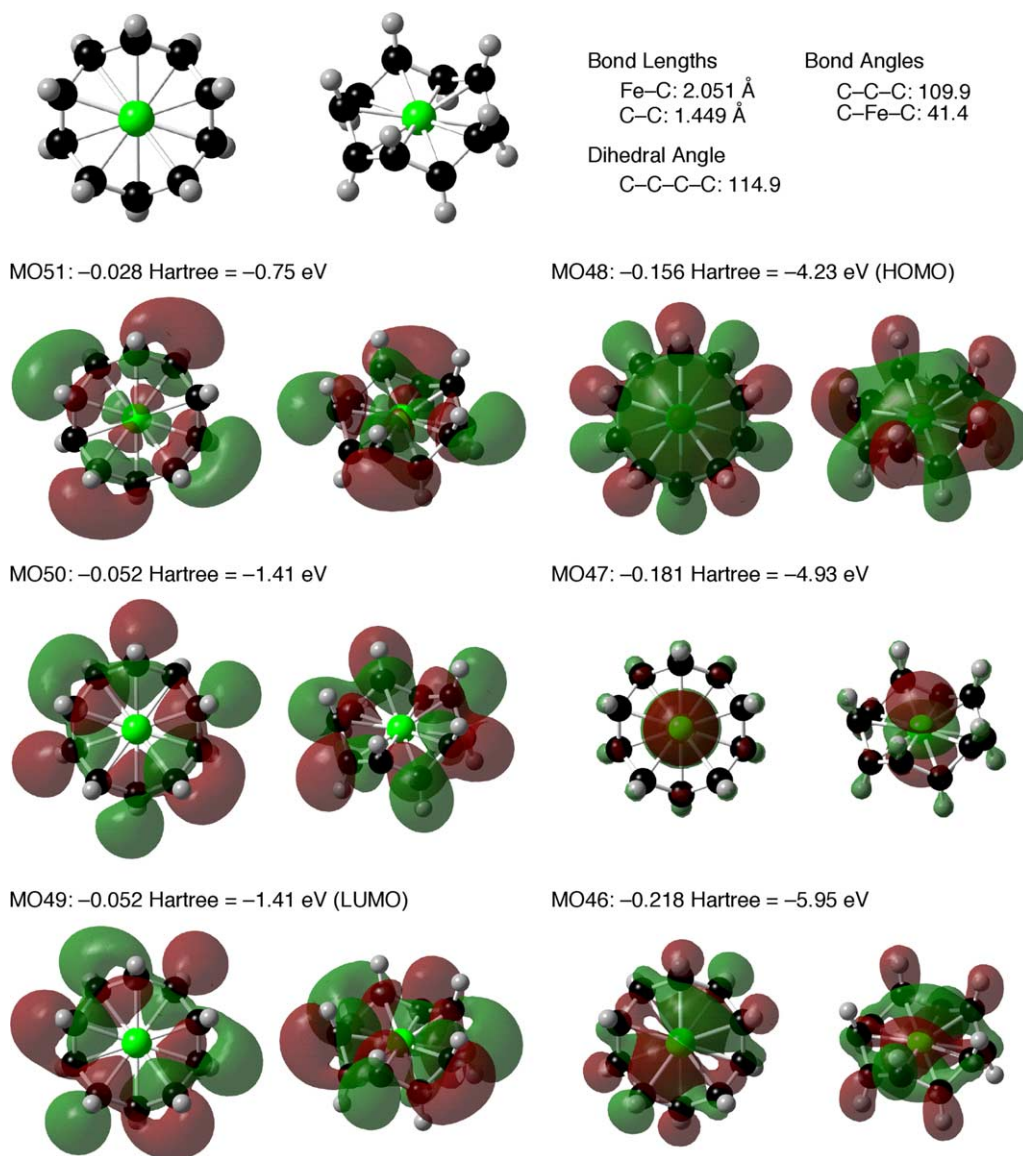


Fig. 1. Fe(DPEN) [B3LYP/6-311+G(2d,p)]. Final geometry optimization was performed by means of the B3LYP hybrid density functional method using a 6-311+G(2d,p) basis set with Gaussian 03.

Table 1  
Optimized structure of the all *trans* DPEN complexes with 18 electron configuration

DPEN complex	Bond length, C–C	Bond length, M–C	Angles, C–C–C	Dihedrals, 2C–C–C–C
Ti(CO) <sub>2</sub> (DPEN)	1.494	2.182	116.0	108.5
[V(CO) <sub>2</sub> (DPEN)] <sup>+</sup>	1.480	2.146	114.5	110.6
CrCl <sub>2</sub> (DPEN)	1.467	2.112	113.5	111.5
Fe(DPEN) (BP86)	1.458	2.060	110.0	115.0
Fe(DPEN) (B3LYP/6-311+G(2d,p))	1.449	2.051	109.9	114.9

The average bond lengths in Å and angles in degrees.

Table 2  
Computed values of HOMO and LUMO of DPEN complexes in BP86 level in Hartree

DPEN complex	HOMO	LUMO	Difference
Ti(CO) <sub>2</sub> (DPEN)	−0.177	−0.138	0.040
[V(CO) <sub>2</sub> (DPEN)] <sup>+</sup>	−0.367	−0.299	0.068
CrCl <sub>2</sub> (DPEN)	−0.202	−0.151	0.051
Fe(DPEN)	−0.135	−0.087	0.048

state, whereas other electronic states (triplet and quintet) were of interest. Generally, due to the thermodynamic stability of the system, the optimization was easily conducted in each case.

It is noteworthy that each of the metals can be placed just at the center of the 10-membered aromatic ring system. The C–C lengths and M–C distances decrease from Ti to Fe as expected. The C–C–C angles also decrease from Ti to Fe, but remain in the region of sp<sup>2</sup> hybridized carbons. The dihedral angles show some deformation from the planarity of olefinic carbons. We also estimated the complexation of DPEN with some 2nd row transition metal fragments such as Nb(CO)<sub>2</sub> and MoCl<sub>2</sub>, and found that the larger size of the 2nd row metals is accommodated without any computational difficulty but with longer C–C bond distance (1.519–1.502 Å). As the bonding schemes are dependent on the d-electron count and co-ligand of the metal, the discussion on the nature of bonding as well as the scope of this type of complexation will be done in later publications.

We tested the combination of magnesium and DPEN as a test case of non-transition metal. Calculation on MgCl<sub>2</sub> and DPEN resulted in sluggish optimization, resulting in the escape of Mg(II) from the cavity of the DPEN. Incorporation of d-orbital for the metal–DPEN system is thus apparent.

Since the DPEN ring has a unique geometry for coordinating to metal, the DPEN complexes would be one of the attracting synthetic targets with a rich variation of functional isomers by substitution on the ring. Though some synthetic attempts have been conceived, no promising route was found at present.

The acetylene analog of the DPEN ligand, i.e., cyclodeca-1,3,5,7,9-pentayne (DPYN), was additionally

examined, though it is expected to be highly unstable. The complexation of DPYN with some vanadium fragments, V(CO)<sub>2</sub> and V(PH<sub>3</sub>)<sub>2</sub>, was computed; however, the C–C and V–C bond distances were not equivalent, indicating that DPYN was not suitable ligand system for transition metals.

In conclusion, we found on the basis of DFT calculation that DPEN is a potential ligand to hold some transition metals in its center. These complexes are unique topological isomers of ferrocene, Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>, and metallocene derivatives. Computational estimation of general properties of the DPEN complexes is of our interest.

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