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**Insight in Structures of Superbulky Metallocenes with the CpBIG Ligand: Theoretical Considerations
of Deca-Phenyl Metallocenes**

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**Insight in Structures of Superbulky Metallocenes with the Cp^{BIG} Ligand:
Theoretical Considerations of Deca-Phenyl Metallocenes****Dennis Kuchenbecker, Sjoerd Harder,* and Georg Jansen*****Keywords:** Metallocenes; density functional calculations; dispersion interactions

The structures of a series of deca-phenyl metallocenes (Ph₅Cp)₂M, which model superbulky metallocenes, are calculated by means of density functional theory including a semi-empirical correction for dispersion interactions (DFT+D). Through a detailed investigation of the calocene it is shown that the interactions between the phenyl substituents of the two cyclopentadienyl ligands lead to a preference of S₁₀-symmetrical structures and that dispersion interactions contribute to the overall stability of superbulky metallocenes.

While the Ph substituents of the two ligands bend away from each other with standard DFT, inclusion of the dispersion correction reproduces the experimentally observed slight inclination towards each other. The experimentally observed linear correlation between the out-of-plane bending angle of the phenyl substituents and the size of the metal atom M (M = Fe, Ni, Cr, W, Ca, Yb, Sn, Sm, Sr, Ba) is also confirmed at the DFT+D level.

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Introduction

Although the superbulky cyclopentadienyl ligand Ph_5Cp is synthetically readily accessible, its use in organometallic chemistry is very limited.^[1] This is largely due to solubility issues. Considerable size and high rigidity and symmetry render its compounds nearly insoluble in any non-reactive organic solvent. Solubility problems can be circumvented by converting the Ph substituents into less rigid groups.^[2, 3] Metallocenes with the ligand $(4-n\text{Bu-C}_6\text{H}_4)_5\text{Cp}$, which on account of its size has been abbreviated as Cp^{BIG} , were found to be well soluble even in apolar solvents like hexane.^[3]

Although metallocenes with bulky Cp ligands generally show strong ligand-ligand repulsion, complexes $(\text{Cp}^{\text{BIG}})_2\text{M}$ were found to be extraordinarily stable. Attempts to prepare the half-sandwich complex $\text{Cp}^{\text{BIG}}\text{CaCH}_2\text{Ph}$ led to ligand exchange and formation of the homoleptic species $(\text{Cp}^{\text{BIG}})_2\text{Ca}$ and $(\text{PhCH}_2)_2\text{Ca}$ (Scheme 1).^[3] More remarkable is the lanthanide chemistry of this ligand: reaction of the Sm(III) complex $(\text{DMA})_3\text{Sm}$ ($\text{DMA} = 2\text{-Me}_2\text{N-benzyl}$) with $\text{Cp}^{\text{BIG}}\text{H}$ did not give the expected half-sandwich compound $\text{Cp}^{\text{BIG}}\text{Sm}(\text{DMA})_2$ but instead the metallocene $(\text{Cp}^{\text{BIG}})_2\text{Sm}$ was isolated.^[3] As the Sm(II) complex Cp^*Sm is even oxidized by molecular nitrogen,^[4] the spontaneous reduction of a Sm(III) precursor to a Sm(II) metallocene is highly unexpected. Although these processes might be in line with *sterically induced reduction* (SIR), a concept recently introduced by Evans,^[5] the unanticipated high stability of metallocenes with the Cp^{BIG} ligand could also play a major role. Although one might expect repulsion between the superbulky Cp^{BIG} ligands, there is considerable evidence for attractive $\text{Ar}_5\text{Cp}\cdots\text{CpAr}_5$ interactions.

Please insert Scheme 1

Scheme 1. Conversion of $\text{Cp}^{\text{BIG}}\text{H}$ into half-sandwich complexes resulted in formation of the metallocene complexes.

(i) The metal-carbon bond distances in metallocenes with the Cp^{BIG} ligand are shorter than expected. *E.g.* the Ba-C bond distances in $(\text{Cp}^{\text{BIG}})_2\text{Ba}$ (average 2.929(2) Å)^[6] are significantly shorter than those in Cp^*Ba (average 2.99(1) Å)^[7] or in $(i\text{Pr}_5\text{Cp})_2\text{Ba}$ (average 2.997(4) Å).^[8] Deacon *et al* reported a similar contraction phenomena for $(\text{Ph}_5\text{Cp})_2\text{Yb}$, which also shows short Cp-metal bonds.^[9]

(ii) As we discussed earlier,^[3, 6] the aryl substituents in the Cp^{BIG} ligands are bent out of the Cp-plane (Figure 1). For smaller metals, substituents bend away from the metal and each other, defined in here with a positive bending angle. For larger metals, bending towards each other is observed, *i.e.* negative bending angles. In fact there is a linear correlation between the Cp-metal distance and the out-of-plane bending angle (*vide infra*). The aryl substituents in $(\text{Cp}^{\text{BIG}})_2\text{Ba}$ bend towards each other with an average angle of $-5.3(2)^\circ$. This contrasts sharply with generally observed repulsive interactions: *e.g.* the *iPr* groups in $(i\text{Pr}_5\text{Cp})_2\text{Ba}$ bend away from each other with an average bending angle of $+5.1(2)^\circ$.^[8]

Please insert Figure 1

Figure 1. Out-of-plane bending of the aryl groups in $(\text{Cp}^{\text{BIG}})_2\text{Ba}$; only the C_{ipso} atoms of the substituents are shown.

Please insert Figure 2

Figure 2. a) The two possible isomers for a deca-aryl metallocene complex. b) The merry-go-round C-H \cdots C(π) hydrogen bond network exemplary shown for $(\text{Cp}^{\text{BIG}})_2\text{Ca}$ (partial structure).

(iii) Without exception, all deca-arylmetallocene complexes crystallize with approximate S_{10} -symmetry.^[6] The penta-aryl Cp ligand can be regarded as a five-blade chiral propeller. Combination of propellers of equal chirality gives a D_5 -symmetric metallocene whereas opposite chiralities result in a S_{10} -symmetric structure (Figure 2a). Both isomers differ by the mutual orientation of the phenyl substituents on different ligands: the S_{10} -symmetric metallocene features perpendicularly interacting phenyl rings whereas the D_5 -isomer shows parallel interacting rings.

We explained the high stability of the S_{10} -symmetric metallocenes with an extended network of interligand C-H \cdots C(π) interactions (Figure 2b).^[3] Especially for small metals, these interactions can be quite short: in $(\text{Ph}_5\text{Cp})_2\text{Fe}^{[10]}$ an average H \cdots C distance of 2.41 Å has been derived.^[11] *i.e.* a H \cdots C contact much shorter than the sum of the van der waals radii for C and H (2.90 Å). Also for metallocenes with larger metals short C-H \cdots C(π) interactions have been detected.^[3, 6] These explain the unusually negative out-of-plane bending angles discussed in (ii).

In order to understand and quantify the unusual stability of deca-aryl metallocenes we here describe the results of a systematic theoretical investigation.

The objectives of this calculational study were the following: (i) Is it possible to reproduce the solid state structure of deca-aryl metallocenes by DFT-methods? (ii) What is the effect of the aryl substituents on structure and the overall energy of formation? (iii) What is the origin of $\text{Ar}_5\text{Cp}\cdots\text{CpAr}_5$ attraction? (iv) Can we reproduce the linear relationship between out-of-plane bending of the aryl substituents and the Cp-metal distance, *i.e.* metal size?

Calculation methods

All calculations have been performed with density functional theory (DFT) methods. The PBE model^[12] has been employed for the exchange-correlation (xc) functional. Since long-range dispersion interactions cannot be accounted for by a purely gradient-corrected functional such as PBE, the level of calculations has been raised to DFT+D through the semi-empirical dispersion correction proposed by Grimme.^[13] Dispersion interactions between the phenyl substituents of the upper and lower Cp^{BIG} ligands were expected to play a crucial role for association energy and molecular structure. On the other hand, the butyl substituents of the benzene rings are not expected to be of importance, they were replaced by hydrogen atoms. All calculations of the resulting $(\text{Ph}_5\text{Cp})_2\text{M}$ systems with $\text{M} = \text{Ba}, \text{Ca}, \text{Cr}, \text{Fe}, \text{Ni}, \text{Sm}, \text{Sn}, \text{Sr}, \text{W},$ and Yb have been carried out with the Turbomole^[14,15] quantum chemistry program package, using an orbital basis set of triple-zeta valence quality denoted as def-TZVP, an appropriate auxiliary basis set to represent Coulomb integrals in the resolution-of-the-identity (RI) approximation and effective core potentials which account for scalar relativistic effects of the heavier metal atoms (Ba, Sm, Sn, Sr, W, Yb).^[16] If not mentioned otherwise, default values were used for energy and gradient convergence thresholds and the size of

numerical integration grids and. Geometry optimizations of closed-shell $(\text{Ph}_5\text{Cp})_2\text{M}$ species have been carried out within the symmetry restrictions of the S_{10} point group using restricted Kohn-Sham orbitals, that of open-shell cases^[17] within its Abelian subgroup C_i using unrestricted orbitals. Partial charges have been taken from natural population analysis (NPA).^[18]

Results and Discussion

The calcocene $(\text{Ph}_5\text{Cp})_2\text{Ca}$ has been taken as model system for closer investigation. In order to evaluate the influence of Ph substituents on the structure, first the simple calcocene Cp_2Ca has been optimized. This compound is a coordination polymer with a bent structure in the solid state.^[19] In agreement with previous studies we find that its calculated gas phase minimum shows a linear arrangement of Ca and the centers of the two Cp rings.^[20] Its staggered (D_{5h}) and the eclipsed (D_{5d}) form are practically isoenergetic: using tight convergence thresholds and a refined integration their energy difference is smaller than 0.01 kJ/mol with both approaches, DFT and DFT+D. Furthermore, the Ca-C bond distances in the staggered and eclipsed forms agree within 10^{-4} Å. According to calculations of the vibrational frequencies with analytical second energy derivatives both structures are minima, with lowest vibration frequencies of 21 (D_{5h}) and 32 (D_{5d}) wavenumbers, respectively, at the PBE+D level. These findings agree with corresponding observations for Cp_2Mg .^[20b] Table 1 shows selected geometric parameters and energies of calcocene formation, ΔE_f , from the free ions Ca^{2+} and Cp^- , with optimized structures for the latter. Note that the dissociation energies of Ref. [20b] refer to dissociation into neutral compounds. Surprisingly, inclusion of the dispersion correction (DFT+D) results in slight lengthening of the Ca-Cp_c distance, *i.e.*, the distance between Ca and the center of the Cp ring, by 0.013 Å. Despite this elongation, the magnitude of ΔE_f increases by 22.2 kJ/mol (1 %). This apparent contradiction is likely to be a minor artefact of the damping scheme introduced by Grimme to avoid double counting of electron correlation effects: the additive dispersion correction including the damping function for a Ca-C pair of atoms starts to become smaller for distances below 3 Å, thus creating a small repulsive force. Obviously, this effect is much smaller for relatively short bond distances such as the C-C distance, where an elongation of only 0.001 Å is observed (*cf.* Table 1). Note also that in both forms (D_{5h} and D_{5d}) of the complex the H atoms bend away from Ca by 2.1° with DFT and by 1.9° with DFT+D, respectively, probably for the same Coulombic reasons as in CpLi.^[21]

Method	ΔE_f	Ca-Cp _c	Ca-C	C-C
DFT	-2098.3	2.345	2.639	1.422
DFT+D	-2120.5	2.358	2.651	1.423

Table 1. Energies of formation from the ions and selected geometric parameters for CaCp_2 from calculations with tight convergence thresholds and refined integration grid. Energies in kJ/mol, distances in Å. Data for eclipsed and staggered structures agree within all digits shown.

The model system $(\text{Ph}_5\text{Cp})_2\text{Ca}$ was optimized within the symmetry restraints S_{10} or D_5 . These correspond to the isomers shown in Figure 2a. Table 2 shows formation energies and selected geometric parameters obtained with

DFT and DFT+D and, for comparison, selected geometric parameters for the crystal structure of $(\text{Cp}^{\text{BIG}})_2\text{Ca}$. The DFT-optimized S_{10} calcocene shows somewhat longer Cp-Ca bonds than the crystal structure. Whereas in Cp_2Ca inclusion of dispersion correction led to elongation of Cp-Ca bonds, for $(\text{Ph}_5\text{Cp})_2\text{Ca}$ a contraction by 0.015 Å is observed. The DFT+D-optimized structure is in close agreement with the crystal structure. The D_5 calcocene shows somewhat longer Cp-Ca distances but also this complex is contracted when the dispersion correction is included. As both calcocenes (S_{10} and D_5) show shortening of Cp-Ca distances upon inclusion of dispersion correction, their structures must be influenced by attractive Ph...Ph interactions.

The S_{10} -metallocene shows the typical perpendicular edge-to-face stacking, as found in the fish-bone structure of solid benzene.^[22] The merry-go-round network, consisting of ten non-classical C-H...C hydrogen bonds, can be considered as a circular form of this fish-bone structure (Figure 2b). It should be noticed that the C-H...C bond distances in the crystal structure (average value: 2.58 Å) are reproduced well by the DFT+D model (2.53 Å). Calculations without dispersion correction gave much longer contacts (2.82 Å). On the other hand, the D_5 -metallocene displays face-to-face stacking of phenyl substituents, a type of interaction that plays an important role in molecular recognition.^[23] Apart from the face-to-face stacking interactions within the propeller-like Ph_5Cp ligand, there are five such interactions between the two ligands. The energies of formation are clearly in favour of the S_{10} -metallocene ($\Delta E = 41.1$ kJ/mol with DFT+D) and explain why deca-aryl metallocenes preferably crystallize as centrosymmetric complexes with approximate S_{10} -symmetry.

The preference for the S_{10} -geometry must be related to the difference and number of Ph...Ph interactions. According to very high level *ab initio* calculations (displaced) face-to-face and edge-to-face structures of the fully relaxed benzene dimer are very nearly isoenergetic (interaction energies of -11.2 and -11.1 kJ/mol for the edge-to-face and face-to-face structures, respectively).^[24] In order to quantify the two different forms of stacking within the metallocenes, we calculated the interaction energies of two benzene molecules with the exact mutual orientations as found in the S_{10} and D_5 structures optimized at the DFT+D level. Without inclusion of the dispersion correction all Ph...Ph interactions were found to be endothermic. With DFT+D the strongly distorted face-to-face interactions within a single Ph_5Cp ligand were found to be slightly exothermic (-0.67 kJ/mol for a pair of Ph substituents in the S_{10} -structure and -0.16 kJ/mol in the D_5 -structure). The edge-to-face interactions between two Ph groups of the upper and lower Ph_5Cp ligands of the S_{10} -structure were found to be -8.72 kJ/mol, the corresponding face-to-face interactions in the D_5 -structure -8.70 kJ/mol. The sum of the ten inter-ligand and ten intra-ligand Ph...Ph interactions gives a total interaction energy of -93.9 kJ/mol for the S_{10} -structure. In the D_5 -structure the number of inter-ligand Ph...Ph interactions is reduced to five. The total interaction energy for all inter- and intra-ligand Ph...Ph interactions amounts to -45.1 kJ/mol. The difference of 48.8 kJ/mol between these numbers is in reasonable agreement with the difference of 41.1 kJ/mol in the formation energies of both structures (*cf.* Table 2). Since the benzene dimer is a relatively small model system we were able to check this explanation for the preference of the S_{10} -structure by increasing the theoretical level considerably to coupled cluster theory at the CCSD(T) level, with an augmented correlation-consistent double-zeta valence basis

set (aug-cc-pVDZ).^[25] These calculations, in which the valence electrons were correlated, were made with the Molpro program package.^[26] Employing exactly the same benzene dimer geometries as above, the counterpoise-corrected interaction energies for the strongly distorted intra-ligand face-to-face orientations were now found to be endothermic (+6.50 kJ/mol for a pair of Ph substituents in the S_{10} -structure and +6.98 kJ/mol in the D_5 -structure). The inter-ligand Ph...Ph interactions remain exothermic: we find -5.25 kJ/mol for the edge-to-face orientation in the S_{10} -structure and -6.86 kJ/mol for the face-to-face orientation in the D_5 -structure. For the total interaction energy between all phenyl substituents one thus gets +12.5 kJ/mol in the former and +35.5 kJ/mol in the latter case, *i.e.* a preference of the S_{10} -structure by 23 kJ/mol due to Ph...Ph interactions at this level of theory. Note that in the limit of complete basis sets the interaction energies of both, edge-to-face and displaced face-to-face structures become more exothermic by about 1.5 kJ/mol as compared to the basis set used here,^[24] suggesting the total Ph...Ph interaction energy in the S_{10} -structure becomes exothermic in the complete basis set limit while that in the D_5 -structure remains endothermic.

It should be noted that for the S_{10} -structure of $(\text{Ph}_5\text{Cp})_2\text{Ca}$ the attractive edge-to-face interactions between the phenyl substituents of both ligands lead to an unusual negative out-of-plane bending angle (*cf.* Table 2) of the aryl substituents, *i.e.* bending towards each other (Figure 1). Without inclusion of the dispersion correction out-of-plane bending is strongly positive. The origin of this bending is therefore related to mutual Ph...Ph interaction. A corresponding reduction of the positive bending angle can also be observed for the D_5 -structure.

Although the data above provide enough evidence for attractive $\text{Ph}_5\text{Cp}\cdots\text{CpPh}_5$ interactions, the energy of formation for S_{10} -symmetric deca-phenyl calocene (-1954 kJ/mol) is considerably smaller than that for Cp_2Ca (-2121 kJ/mol). It is likely that formation of $(\text{Ph}_5\text{Cp})_2\text{Ca}$ from its ions (Ca^{2+} and Ph_5Cp^-) is less exothermic on account of delocalization of negative charge in the Ph_5Cp^- ion. Although the Ph substituents are for steric reasons not completely coplanar with the Cp ring, the average dihedral angle of about 45° allows for partial delocalization of negative charge over the Ph substituents. Indeed, NPA-analysis of the Ph_5Cp^- ion shows charges of $-0.11 e$ on each Ph-substituent. This leaves a charge of $-0.45 e$ on the C_5 ring. In contrast, the calculated NPA-charge on each of the H atoms of the Cp^- ion is $+0.17 e$ and the total charge on the C_5 ring $-1.85 e$. Therefore, the electrostatic $\text{Cp}^--\text{Ca}^{2+}$ interaction is preferred. It should be mentioned that combining the Ph_5Cp^- ion with Ca^{2+} leads to polarization of negative charge into the C_5 ring, which now displays an NPA-charge of $-0.79 e$ while the Ph-substituents become nearly neutral ($-0.01 e$). A similar, yet somewhat weaker effect is observed for Cp^- in Cp_2Ca : in the complex the charge on the C_5 ring is $-2.03 e$ and that on each of the H atoms $+0.23 e$. The NPA charge on the Ca^{2+} ion is very similar in both calocenes: in Cp_2Ca it is $+1.76 e$ and in $(\text{Ph}_5\text{Cp})_2\text{Ca}$ $+1.72 e$.

Experimentally, we found a linear correlation between bending angle and Cp-M distance for a series of deca-phenyl metallocenes (*vide supra*).^[6] In order to confirm the observed dependence between bending angle and metal size, a set of geometry optimizations was carried out for the experimentally investigated species. Results are collected in Table 3. Clearly, there is the expected strong correlation between energy of formation and charge of the metal cation. For species of the same charge, there is roughly an inverse

relation between the energy of formation and the M-Cp_c distance, *i.e.* metal size. As demonstrated by deca-phenyl stannocene and ytterbocene, however, electronic factors modify this grossly simplifying picture. Nevertheless, Figure 3 shows that there is an approximately linear relationship between the out-of-plane bending angle and the Cp-M distance. It can also be seen that the theoretical calculations are in close agreement with the experimentally found dependence.

Please insert Figure 3

Figure 3. Correlation between the out-of-plane bending angle $\text{C}_{\text{Cp}}\text{Cp}\text{C}_{\text{Cp}}$ of the substituents and the M-Cp_c distance. Filled squares denote experimental data, open squares calculated data.

Conclusions

Our detailed investigation of $(\text{Ph}_5\text{Cp})_2\text{Ca}$ via DFT calculations, including and excluding a semi-empirical correction for dispersion interactions, shows that the preference of S_{10} -symmetrical structures is mainly due to inter-ligand Ph...Ph interactions. Dispersion interactions play an important role for the relative and the overall stability of superbulky metallocenes. While the phenyl substituents of the two Ph_5Cp ligands in $(\text{Ph}_5\text{Cp})_2\text{Ca}$ bend away from each other with standard DFT, inclusion of the dispersion correction in DFT+D reproduces the experimentally observed slight inclination towards each other.

In the crystal structures of $(\text{Ph}_5\text{Cp})_2\text{M}$ one observes a linear correlation between the out-of-plane bending angle of the phenyl substituents and the size of the metal atom M along the series $\text{M} = \text{Fe}, \text{Ni}, \text{Cr}, \text{W}, \text{Ca}, \text{Yb}, \text{Sn}, \text{Sm}, \text{Sr},$ and Ba . This trend was confirmed at the DFT+D level. Thus dispersion interactions are the key to their quantitative and qualitative understanding.

Supporting Information (see footnote on the first page of this article): Coordinates and energies of the optimized structures. Vibration frequencies for Cp_2Ca .

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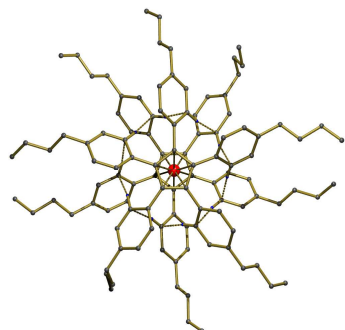
Table 2. Calculated energies of formation and selected geometrical parameters for (Ph₅Cp)₂Ca. Experimental data were averaged. Energies in kJ/mol, distances in Å, angles in degrees.

Conformer	Method	ΔE _f	Ca-Cp _c	Ca-C	C _{ipso} -C _{Cp} ∠Cp	H...C	C-H...C
S ₁₀	Exp.		2.356	2.651	-1.21	2.58	155
	DFT	-1822.8	2.368	2.665	+3.0	2.82	162
	DFT+D	-1954.1	2.352	2.650	-2.2	2.53	154
D ₅	DFT	-1803.1	2.388	2.683	+4.7		
	DFT+D	-1913.0	2.365	2.661	+1.1		

Table 3. Calculated (DFT+D) energies of formation and selected geometrical parameters for (Ph₅Cp)₂M. Experimental data (in parentheses) were averaged. Energies in kJ/mol, distances in Å, angles in degrees.

Complex	ΔE _f	M-Cp _c	M-C	C _{ipso} -C _{Cp} ∠Cp	H...C	C-H...C
[(Ph ₅ C ₅) ₂ Fe]	-2652.5	1.710	2.106	+9.2	2.32	174
		(1.724)	(2.12)	(+11.4)	(2.41)	(173)
[(Ph ₅ C ₅) ₂ Ni] ⁺	-5741.5	1.816	2.194	+7.2	2.35	170
		(1.839)	(2.204)	(+8.4)	(2.43)	(167)
[(Ph ₅ C ₅) ₂ Cr] ⁺	-5096.5	1.915	2.274	+5.5	2.37	168
		(1.932)	(2.281)	(+7.2)	(2.45)	(168)
[(Ph ₅ C ₅) ₂ W] ⁺	-4617.1	2.042	2.384	+4.3	2.46	166
		(2.018)	(2.357)	(+6.2)	(2.49)	(171)
[(Ph ₅ C ₅) ₂ Yb]	-1874.9	2.340	2.639	-1.6	2.56	155
		(2.382)	(2.673)	(-1.4)	(2.61)	(154)
[(Ph ₅ C ₅) ₂ Sn]	-2174.6	2.427	2.717	-2.0	2.60	155
		(2.401)	(2.691)	(-1.2)	(2.68)	(160)
[(Ph ₅ C ₅) ₂ Sm]	-1794.1	2.466	2.751	-3.5	2.62	151
		(2.505)	(2.782)	(-3.5)	(2.67)	(154)
[(Ph ₅ C ₅) ₂ Sr]	-1826.6	2.530	2.808	-5.2	2.60	149
		(2.513)	(2.790)	(-3.4)	(2.69)	(152)
[(Ph ₅ C ₅) ₂ Ba]	-1627.9	2.685	2.948	-6.8	2.76	146
		(2.667)	(2.929)	(-5.3)	(2.81)	(149)

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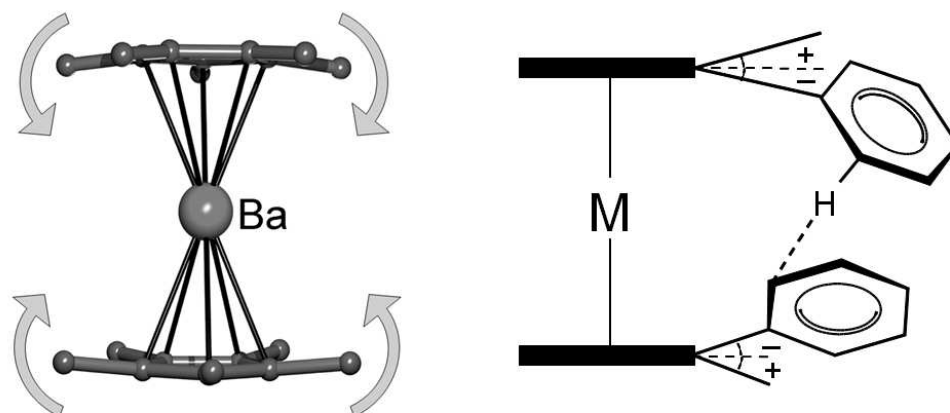


Dennis Kuchenbecker, Sjoerd Harder*, and Georg Jansen*

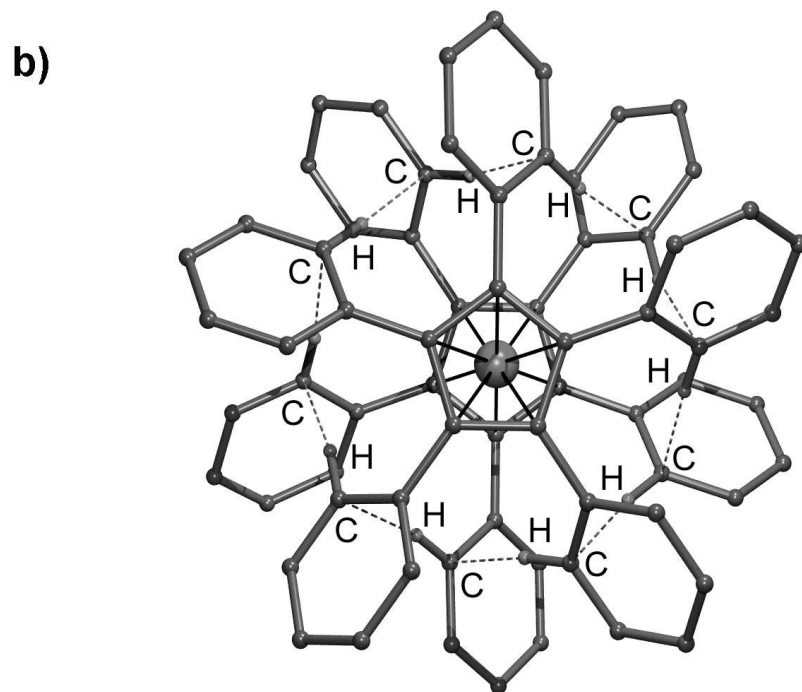
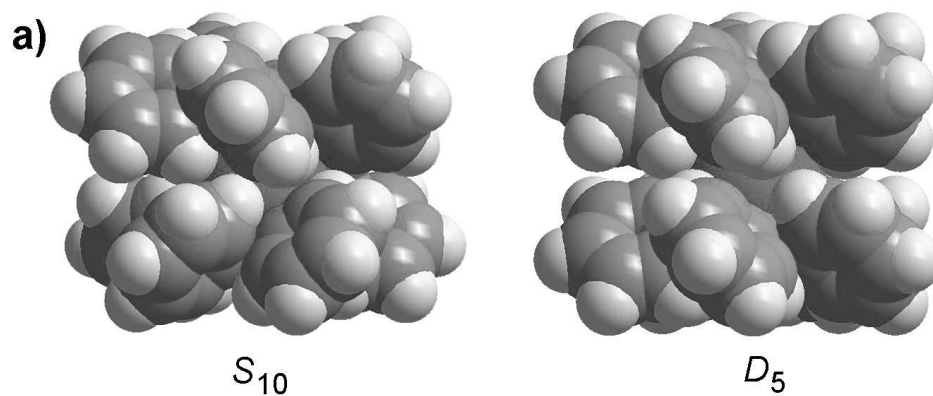
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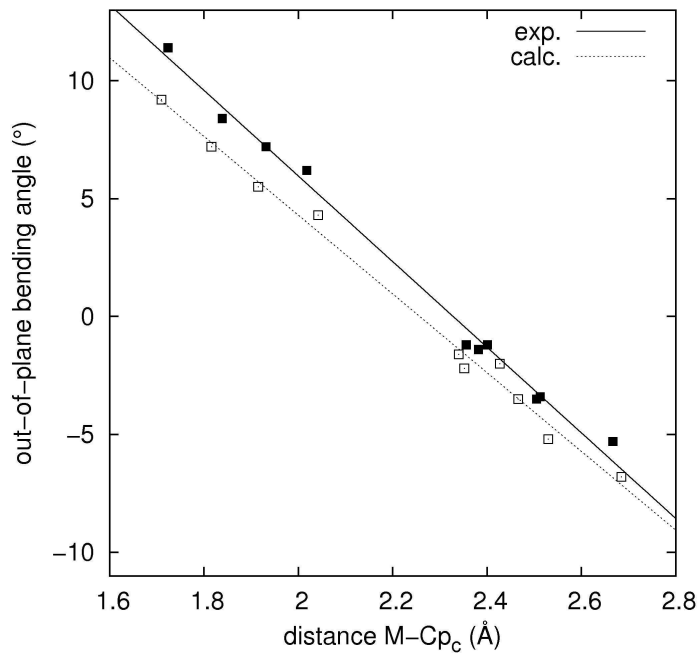
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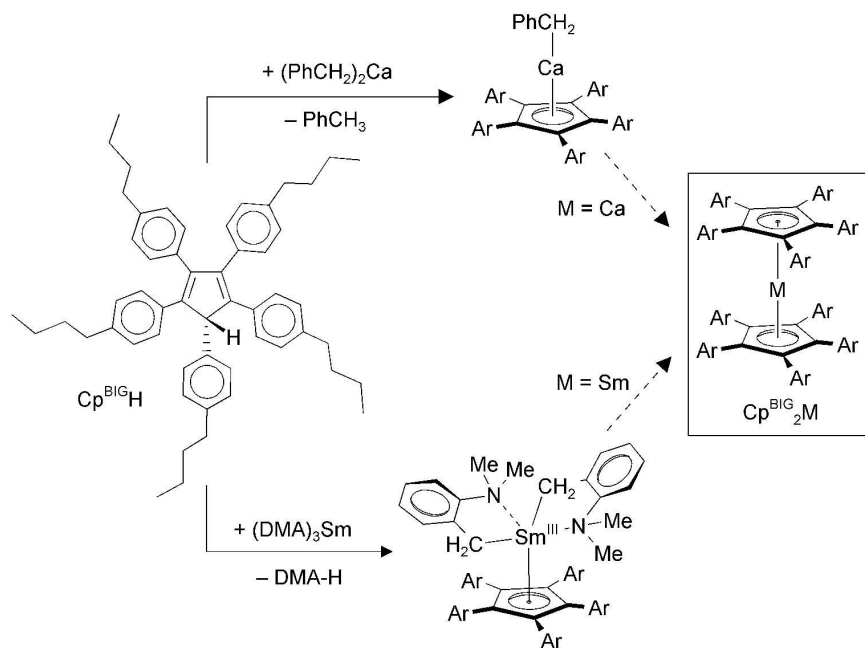
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