

**Winter School in  
Theoretical Chemistry 2009**

**CHEMICAL BONDING**

**December 14-17, 2009**

**Helsinki, Finland**

## Program

Monday 14.12		Tuesday 15.12		Wednesday 16.12		Thursday 17.12	
		09:00	Frenking 3	09:00	Frenking 4	09:00	Dognon
09:15	Welcome	09:45	Wagner 2	09:45	Pyykkö 2	09:45	Andrews
09:30	Schmidt 1	10:30	Break	10:30	Break	10:30	Break
10:15	Schmidt 2	11:00	Pyykkö 1	11:00	Pyykkö 3	11:00	Sundholm 2
11:00	Break	11:45	Luch	11:45	Sundholm 1	11:45	Luch
11:30	Frenking 1	13:00	Lundell 1	13:00	Lunch	13:00	Lecture 22
12:15	Lunch	13:45	Lundell 2	Free afternoon		13:45	Lecture 23
13:15	Frenking 2	14:30	Break			14:30	Departure
14:00	Kaupp 1	15:00	Knowles 1				
14:45	Break	15:45	Knowles 2				
15:15	Kaupp 2						
16:00	Wagner 1						
16:45	Poster session						
		17:00	CCS				

CCS = Meeting of the Computational Chemistry Section of The Association of Finnish Chemical Societies.

# Poster Abstracts

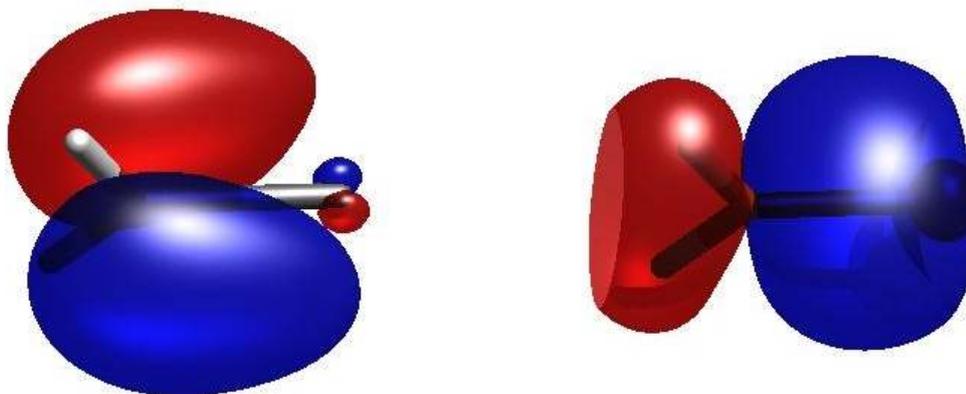
# Molecular Double-Bond Covalent Radii for Elements Li-E112

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The previous systems of triple-bond[1] and single-bond[2] self-consistent, additive covalent radii,  $R(AB) = r(A) + r(B)$ , are completed with a fit for  $\sigma^2\pi^2$  double-bonds.

The primary bond lengths,  $R$ , are taken from experimental or theoretical data corresponding to chosen group valencies. All  $r(E)$  values are obtained from the same, self-consistent fit. Many of the calculated primary data came from  $E=CH_2$  and  $H-E=CH_2$  models. Homonuclear  $LE=EL$ , formaldehyde-type Group 14– Group 16 and open-shell,  $X^3\Sigma$  Group- 16 dimer data are included. The standard deviation for the 316 included data points is 3 pm.



The two (MP2) valence orbitals of  $H_2C=Mg$ .

- [1] P. Pyykkö, S. Riedel and M. Patzschke, *Chem. Eur. J.*, **11**, 3511 (2005)
- [2] P. Pyykkö and M. Atsumi, *Chem. Eur. J.*, **15**, 186 (2009)
- [3] P. Pyykkö and M. Atsumi, *Chem. Eur. J.*, **15**, 12770 (2009)

# Theoretical pKa calculations of substituted pyridines

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Theoretical pKas are usually obtained considering thermodynamic cycles which also can involve some experimental values as solvation free energies for proton, water and hydronium. We considered three different cycles which combine gas phase and liquid phase calculations. Gas phase deprotonation free energies and aqueous solvation free energies were calculated using CBS-QB3 and HF/CPCM or B3LYP/CPCM methods. In this work, we report the ab initio and DFT pKa theoretical predictions for 2-, 3-, 4- hydroxypyridines and 2-, 3-, 4- pyridinecarboxylic acids. Results show that the inclusion of explicit single water molecule interacting with pyridine nitrogen improves predictions in 1.5 pKa units. Water molecule causes an increase in the solute-solvent surface interaction and allows the continuum method to reproduce correct solvation free energy differences between acids and bases. The correct combination of quantum methodology and thermodynamic cycle leads to very accurate results, with mean absolute errors of 0.3-0.5 pKa units for monoprotic and 0.7-0.9 pKa units for diprotic pyridines.

## Ab-initio study of magnetic exchange coupling constants of square-pyramidal $\text{Co}_5^{\text{II}}$ complexes

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Recently Powell *et. al.* managed to synthesize a set of square-pyramidal  $\text{Co}_5^{\text{II}}$  complexes [1]. A simplified Heisenberg model Hamiltonian with three independent constants was applied to extract the magnetic spin coupling constants  $J_{ij}$ . It was shown that small variations in the ligand shell modify not only the magnitude of the exchange constants, but also affect the  $g$  tensors in a non-trivial way [1].

A recent study of the magnetic exchange couplings of a mixed valent  $\text{Mn}_4$  complex showed that the modified complete active space configuration interaction approach (MCI) [2] leads – compared to DFT broken symmetry [3] results – to the best agreement with the experiment although the four center problem was cut into two center clusters [4]. In the present study the exchange coupling constants of the respective  $\text{Co}_5^{\text{II}}$  complexes are investigated at the DFT broken symmetry and MCI level to understand the influence of the ligand sphere on the magnetic properties. The full Heisenberg Hamiltonian of the five center problem is used to calculate the magnetic susceptibilities, which are compared to experimental values. It will be shown that the correct description of the  $g$  tensors is essential for the present problem.

- [1] F. Klöwer, Y. Lan, J. Nehr Korn, O. Waldmann, C. E. Anson and A. K. Powell, *Chem. Eur. J.*, 7413 (2009)
- [2] K. Fink, *Chem. Phys.*, **326**, 297 (2006)
- [3] L. Noodleman, *J. Chem. Phys.*, **74**, 5757 (1981)
- [4] H. Fliegl, K. Fink, W. Klopper, C. E. Anson, A. K. Powell and R. Clérac, *Phys. Chem. Chem. Phys.*, **11**, 3900 (2009)

# Chemical Bonding in Transition Metal Borylene Complexes - an ELF and AIM Study

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A survey of bonding patterns in terminal and bridged transition metal borylene complexes is given employing ELF and QTAIM techniques.[1] By means of topological analysis, different metal-boron interaction types are distinguished with respect to the spin state of the boron atom and the nature of the transition metal. In view of the classification of transition metal **carbene** complexes via the scheme of Fischer and Schrock, carbene and borylene species are compared.

[1] K. Goetz, M. Kaupp, H. Braunschweig, D. Stalke Chem. Eur. J. **15**, 623 (2009). H. Braunschweig, B. Christ, M. Colling-Hendelkens, M. Forster, M. Kaupp, K. Radacki, F. Seeler Chem. Eur. J. **15**, 7150 (2009).

# A simplified model for spin-orbit excitation of Cl substitutional impurities in parahydrogen matrices

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Solid parahydrogen (pH<sub>2</sub>) matrices containing open-shell (<sup>2</sup>P) Cl and Br atoms as substitutional impurities exhibit several infrared (IR) absorption features associated with intermolecular interactions between the halogen atom and nearby pH<sub>2</sub> molecules [1, 2]. These dopant-induced IR absorption features are associated with (i) spin-orbit (SO) excitation of the halogen atom, and (ii) cooperative excitations in which a single IR photon both triggers SO excitation of the halogen atom and excites the H-H stretching coordinate of a nearby pH<sub>2</sub> molecule. The IR spectral features thus contain detailed information about the interaction between the open-shell halogen atom and the surrounding pH<sub>2</sub> molecules, and in particular tell us about the coupling between the atom's electronic degrees of freedom and the nuclear motion of its H<sub>2</sub> neighbors.

Here we present initial steps towards decoding the Cl-induced features in the IR absorption spectrum of Cl-doped solid pH<sub>2</sub>. This system represents a prototypical arena for testing theoretical approaches for combining multiple low-lying Cl-H<sub>2</sub> pair potential energy surfaces [3] to generate non-pairwise-additive many-body interactions describing the open-shell Cl atom's interaction with many nearby pH<sub>2</sub> molecules. In this poster presentation, we use a reduced dimensionality model to understand how the electronic degrees of freedom of the Cl dopant is coupled to the rotational degrees of freedom of neighboring pH<sub>2</sub> molecules.

[1] P.L. Raston and D.T. Anderson, *J. Chem. Phys.* **126**, 021106 (2007).

[2] S.C. Kettwich, L.O. Paulson, P.L. Raston, and D.T. Anderson, *J. Phys. Chem. A* **112**, 11153 (2008).

[3] G. Capecchi and H.-J. Werner, *Phys. Chem. Chem. Phys.* **6**, 4975 (2004).

# Chemical Bonding in Mo(ZnH)<sub>12</sub> and Other Icosahedral Compounds

Moritz von Hopffgarten and Gernot Frenking

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With R. A. Fischer *et al.* we reported the synthesis of Mo(ZnCp<sup>\*</sup>)<sub>3</sub>(ZnMe)<sub>9</sub> (**1**) with a slightly distorted icosahedral MoZn<sub>12</sub> core and an analysis of the bonding situation of its perfectly icosahedral parent compound Mo(ZnH)<sub>12</sub> (**1H**) [1]. For the discussion of the nature of the chemical bond we applied Molecular-Orbital- (MO), Atoms-in-Molecules- (AIM) [2] and the Energy Decomposition Analysis (EDA) that had been developed by Morokuma [3] and Ziegler and Rauk [4].

MO-, AIM- and EDA of **1H** suggest that chemical bonding in the 18 valence electron compound **1H** may be described as the interaction of a *sd*<sup>5</sup>-hybridised Mo-atom forming six 2-electron-3-center Zn-Mo-Zn bonds pointing at opposing corners of the icosahedron and that Zn-Zn interactions are very weak. In this poster we compare this situation with chemical bonding in the charged isoelectronic compounds [Tm<sup>q</sup>(ZnH)<sub>12</sub>] (Tm<sup>q</sup> = Zr<sup>2-</sup>, Nb<sup>-</sup>, Tc<sup>+</sup>, Ru<sup>2+</sup> and Rh<sup>3+</sup>) and in the icosahedral WAu<sub>12</sub> and MoAu<sub>12</sub> compounds that were predicted Pyykkö and Runeberg [5] and characterized theoretically [6] and experimentally [7].

- [1] (a) T. Cadenbach, T. Bollermann, C. Gemel, I. Fernández, M. von Hopffgarten, G. Frenking and R. A. Fischer, *Angew. Chem. Int. Ed.* 47 (2008) 9150; (b) T. Cadenbach, T. Bollermann, C. Gemel, M. Tombul, I. Fernández, M. von Hopffgarten, G. Frenking and R. A. Fischer, *J. Am. Chem. Soc.* 131 (2009) 16063.
- [2] R. F. W. Bader, *Atoms in Molecules. A Quantum Theory*, Oxford University Press 1990.
- [3] K. Morokuma, *J. Chem. Phys.* 55 (1971) 1236.
- [4] T. Ziegler, A. Rauk, *Theor. Chim. Acta* 46 (1977) 1.
- [5] P. Pyykkö, N. Runeberg, *Angew. Chem. Int. Ed.* 41 (2002) 2174.
- [6] J. Autschbach, B. A. Hess, M. P. Johansson, J. Neugebauer, M. Patzschke, P. Pyykkö, M. Reiher, D. Sundholm, *Phys. Chem. Chem. Phys.* 6 (2004) 11.
- [7] X. Li, B. Kiran, J. Li, H. Zhai, L. Wang, *Angew. Chem. Int. Ed.* 41 (2002) 4786.

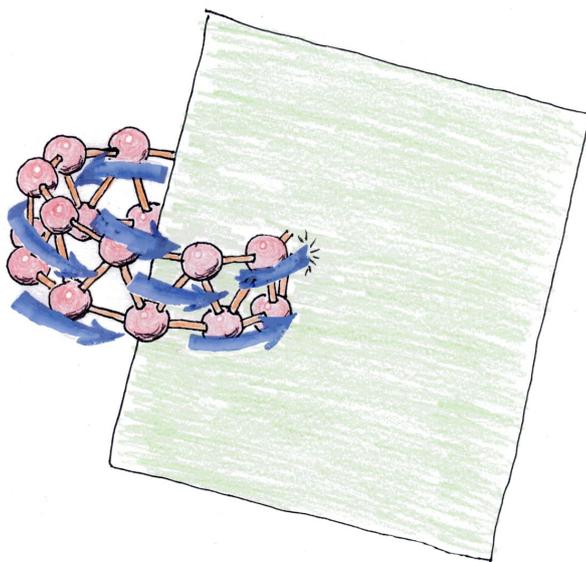
# On the high aromaticity of B<sub>20</sub> and neighbouring boron toroids

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The neutral form of B<sub>20</sub> was recently suggested to be a highly symmetric, beautiful double ring [1], marking the onset of true three-dimensionality for small, neutral boron clusters. Here, the magnetically induced ring currents in the toroidal, double ring forms of the boron clusters B<sub>n</sub>;  $n = 16, 18, 20, 22, 24$  are investigated using quantum chemical methodology, within the Gauge Including Magnetically Induced Currents (GIMIC) framework [2]. B<sub>16</sub>, B<sub>20</sub> and B<sub>24</sub> are found to sustain high diamagnetic currents in their toroidal forms, and are, according to the magnetic criterion of aromaticity, superaromatic; B<sub>18</sub> and B<sub>22</sub>, on the other hand, appear to be strongly anti-aromatic [3].



Schematic of the induced current flow in B<sub>20</sub>

- [1] B. Kiran, S. Bulusu, H.-J. Zhai, S. Yoo, X.C. Zeng, and L.-S. Wang, “Planar-to-tubular structural transition in boron clusters: B<sub>20</sub> as the embryo of single-walled boron nanotubes”, *Proc. Natl. Acad. Sci.* **102**, 961–964 (2005)
- [2] J. Jusélius, D. Sundholm, and J. Gauss, “Calculation of current densities using gauge-including atomic orbitals”, *J. Chem. Phys.* **121**, 3952–3962 (2004)
- [3] M.P. Johansson, “On the Strong Ring Currents in B<sub>20</sub> and Neighboring Boron Toroids”, *J. Phys. Chem. C* **113**, 524–530 (2009)

# **A detailed DFT study of the mechanism of benzocyclobutene formation by C(sp<sup>3</sup>)-H activation of 2-chloro-*tert*-butylbenzene, catalyzed by monophosphine-palladium complexes.**

*Eric Clot and Christos E. Kefalidis*

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## ***Abstract***

A comprehensive and consistent picture of the catalytic cycle of benzocyclobutene formation by 2-chloro-*tert*-butylbenzene catalyzed by Pd(P<sup>*t*</sup>Bu<sub>3</sub>) and a base, has been derived by means of electronic structure calculations at the B3PW91 level of theory. Two possible reaction pathways have been fully explored and the preferred one consists of the following steps:

- 1) Oxidative addition of the chlorobenzene to the monophosphine palladium complex;
- 2) coordination of the base (carbonate) followed by a barrierless dissociation of the chloride;
- 3) base assisted C(sp<sup>3</sup>)-H activation of the <sup>*t*</sup>Bu group via a six-membered transition state;
- 4) dissociation of the protonated base to form an unsaturated five-membered palladacycle;
- 5) product formation by C-C coupling.

The activation barrier for the C-C coupling was found to be lower than the one for C-H cleavage, and the latter is the rate-determining step of the entire catalytic cycle, in agreement with previous experimental observations.<sup>1</sup>

<sup>1</sup>M. Chaumontet, R. Piccardi, N. Audic, J. Hitce, J-L. Peglion, E. Clot, and O. Baudoin *J. Am. Chem. Soc.* **2008**, *130*, 15157.

# Conformational comparison of aza- $\beta^3$ -amino acid containing peptidomimetics with parent peptide.

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Favorable conformations of congeners of protein kinase A substrate RRASVA, where all amino acids were consecutively replaced by their aza- $\beta^3$  derivatives, were calculated by using Spartan 4.0 software suite (Wavefunction, Inc.). Conformational searches were performed by using molecular mechanics with additional condition of aqueous medium for founding of stable geometry. All peptides were presented as zwitterions and side chains of arginines were positive charged. Figure 1. is illustrated comparisons between parent peptide RRASVA and peptidomimetics. Insertion aza- $\beta^3$  amino acids into peptide are introduced additional conformational changes in backbone of peptidomimetics compare with parent peptide. The results were compared with experimental data about the phosphorylation reaction of all these peptidomimetic substrates, to specify the role of the peptide backbone structure in substrate recognition process in the enzyme active center.

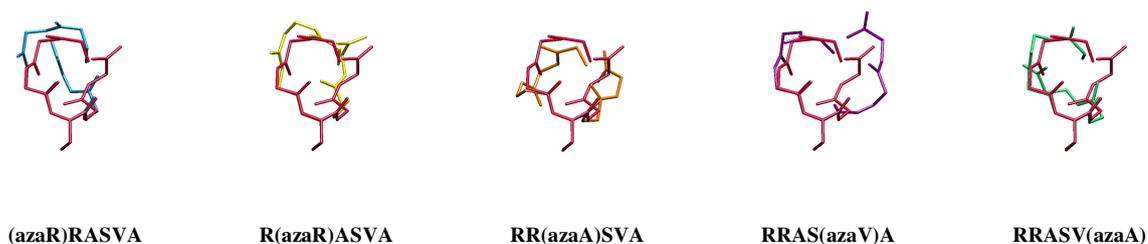


Figure 1. Conformational comparison of parent peptide RRASVA (red) and aza- $\beta^3$  derivatives (other colors).

# **Optical Properties of Oxygen Containing Silicon Nanoclusters**

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Light emitting silicon nanoclusters have been studied extensively during recent years. However, the actual mechanism responsible for the strong optical activity of the nanoclusters has remained unsolved. We have studied small oxygen containing silicon nanoclusters in order to investigate the role of oxygen in the luminescence process. The results are also compared to previously reported many-body perturbation theory based studies.

# **Towards understanding mechanism of reversible H<sub>2</sub> storage: Theoretical study of Ti and Sc catalysed dehydrogenation of NaAlH<sub>4</sub>.**

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On the basis of density functional theory and coupled cluster calculations we propose a mechanism of dehydrogenation of transition metal doped sodium alanate. Two early transition metals, scandium and titanium, are compared, both of which are among the most promising catalysts for reversible hydrogen storage in light metal hydrides. The mechanism is deduced from studies on decomposition of a simple model system consisting of one transition metal atom and two NaAlH<sub>4</sub> units. Subsequently, the significance of such minimal cluster model systems to the real-world materials is tested by embedding the model systems into the surface of the NaAlH<sub>4</sub> crystal. It was found that the dehydrogenation proceeds via intermediate coordination compounds in which the hydrogen molecule is side-on (hapto-) bonded to the transition metal centre. The overall barrier to the H<sub>2</sub> release is thus dependent upon both, the strength of the Al-H bond to be ruptured and the depth of the coordinative potential. The analogous mechanism applies for the recognized three successive dehydrogenation steps. The gas-phase model structures embedded into the surface of the NaAlH<sub>4</sub> slab exhibit an unambiguous kinetic stability and their general geometric features remain largely preserved.

# Accurate electrostatic potentials for periodic systems

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The Direct Approach to Gravitation and Electrostatics (DAGE) algorithm is an accurate, efficient, and flexible method for calculating electrostatic potentials. We show that the algorithm can be easily extended to consider systems with many different kinds of periodicities, such as crystal lattices, surfaces, or wires. The accuracy and performance are nearly the same for periodic and aperiodic systems. The electrostatic potential for semi-periodic systems, namely defects in crystal lattices, can be obtained by combining periodic and aperiodic calculations. The method has been applied to an ionic model system mimicking NaCl, and to a corresponding covalent model system.

# Modelling the CO<sub>2</sub>-over-N<sub>2</sub> selectivity in Zeolite A

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Carbon Capture and Storage (CCS) techniques are predicted to play a decisive role in the need to substantially decrease the industrial CO<sub>2</sub> discharge and slow down the predicted global warming. In the process of carbon capture the separation of CO<sub>2</sub> from N<sub>2</sub> is a crucial step.

Zeolites are crystalline microporous aluminosilicates with interconnected cages or channels. They are used as adsorbents for various gas separation processes, due to their excellent adsorption/diffusion properties, and relatively low cost of production. Zeolites with specific window apertures, such as those of zeolite A, coincide with the approximate size of small gaseous molecules.

Recently, we have achieved very promising experimental results with zeolite A. By fine-tuning the size of the windows through cation exchange a CO<sub>2</sub>-over-N<sub>2</sub> selectivity of >400 has been measured. We believe that at a specific ratio the qualitative pore size allows for a sieving effect between the two gas molecules with very similar kinetic diameters resulting in a much higher separation than similar systems which depend only on thermodynamic effects. A counterintuitive but since long established fact is that the kinetic diameter of CO<sub>2</sub> is approximately 0.3 Å smaller than that of N<sub>2</sub>.

In a modelling approach it is necessary to look at both thermodynamic as well as kinetic models as both effects contribute to the task. Monte Carlo (MC) methods are commonly used when simulating the gas uptake in zeolites<sup>1,2,3</sup>. When simulating the adsorption isotherms with MC a higher uptake of both gases is predicted. These overestimations fall in the line of the thesis where the kinetic effects play a significant role in the separation of the gases as MC does not take these into account.

To provide a more complete picture of the dynamics involved we are currently working with a Molecular Dynamics approach where the kinetic effects can be probed as well as Ab-initio calculations at the specific adsorption sites in order to retrieve more information on the bonds.

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<sup>1</sup> Akten, E. D.; Siriwardane, R.; and Sholl, D. S., *Energy & Fuels* **2003**, *17*, 977-983

<sup>2</sup> Jamarillo, E. and Chandross, M., *J. Phys. Chem. B*, **2004**, *108* (52), 20155-20159

<sup>3</sup> Pillai, R. S.; Peter, S. A. and Jasra, R. V., *Langmuir*, **2007**, *23* (17), 8899-8909

# $\lambda$ -S potential curves and spectroscopic properties of IO: effect of spin-orbit coupling

Katarína MEČIAROVÁ<sup>a</sup>, LUKÁŠ DEMOVIČ<sup>a</sup>, and IVAN ČERNUŠÁK<sup>a</sup>

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Potential energy curves (PEC's), spectroscopic constants, equilibrium geometries and dissociation energies were calculated for the ground and excited states of iodine oxide using the complete active space second-order perturbation theory (CASSCF/CASPT2) and coupled cluster theory through quasiperturbative triple excitations (CCSD(T)), implemented in the MOLCAS 7.3 program package. The ground state of IO( $X^2\Pi$ ) were computed at the CCSD(T) level. Potential energy curves for excited states of IO, which have multi-configuration nature, were computed at the CASSCF/CASPT2 level. The second order spin-free Douglas-Kroll-Hess Hamiltonian was applied to calculate relativistic effects within the spin-adapted CCSD(T) and the CASPT2 method. To include spin-orbit effects, which are important for both ground and excited state of IO due to the presence of the heavy I, we imposed the Restricted Active Space State Interaction method (CASPT2/RASSI-SO), introduced by Roos and Malmqvist [1].

Two active spaces were used in the CASPT2 spin-free calculations for IO: the first consisted of 9 valence electron in 6 orbitals (16a/10b inactive and 2a/4b active), followed by CASPT2 calculations with 17 correlated electrons; the second included 9 valence electron in 12 orbitals (16a/10b inactive and 6a/6b active). A relativistic basis set, ANO-RCC with large contraction (for iodine (22s19p13d5f3g)/[10s9p8d5f3g] and for oxygen (14s9p4d3f2g)/[8s7p4d3f2g]) has been used in all the calculations.

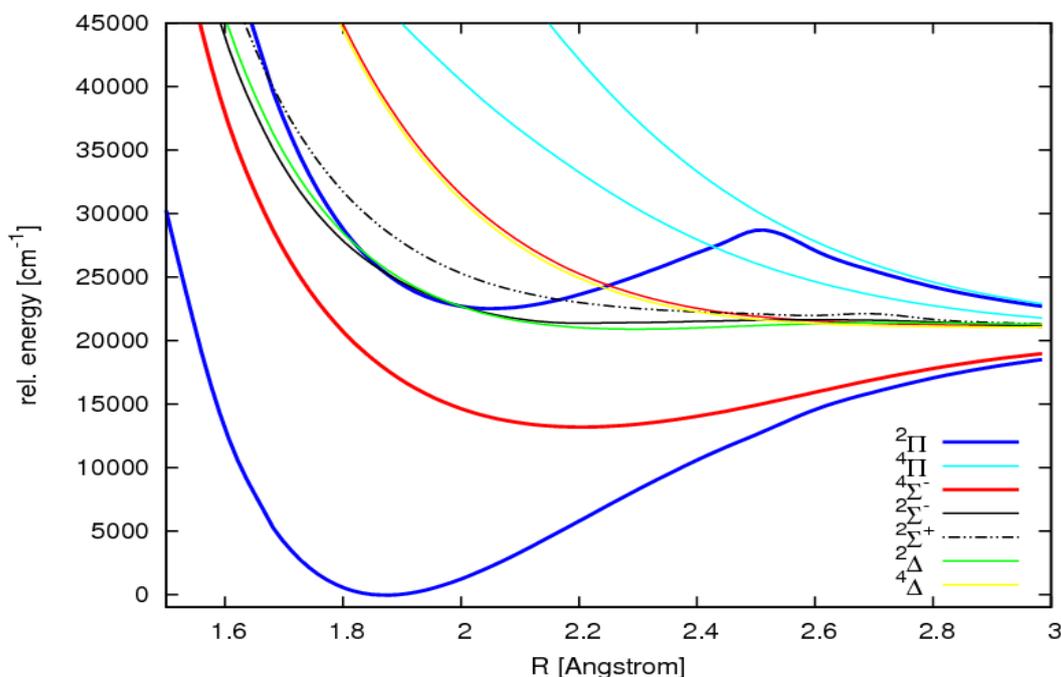


Figure 1: Potential energy curves for ground and excited states of IO molecule

[1] B. Roos and P.-A. Malmqvist, *Phys. Chem. Chem. Phys.*, **6**, 2919 (2004).

# DFT-based Analyses of a Trimetallic Gold Boride Complex with a Fluxional Gold-Boron Bond

Robert Müller, Holger Braunschweig, Peter Brenner, Rian D. Dewhurst, Martin Kaupp, Sebastian Östreicher

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Boron-based ligands are nowadays well established in transition-metal chemistry. Yet the field remains in the focus of intense research, for instance in the context of applications in metal-mediated functionalization of organic compounds [1]. However, stable compounds containing gold-boron bonds are rare, and progress has only been achieved in the last couple of years with the synthesis of two novel gold-boron coordination modes. In these complexes boron is acting either as  $\sigma$ -donor or  $\sigma$ -acceptor [2,3].

Recently, Braunschweig and co-workers succeeded in the synthesis of a trimetallic complex containing a Mn<sub>2</sub>AuB framework. The addition of an anionic metalloborylene to an [AuCl(N-heterocyclic carbene)] complex results in attack of the boron atom at the gold center. Based on density functional theory studies, the electronic structure of this complex has been analyzed in detail. Together with experimental NMR spectroscopy and X-ray structure data, the calculations show that the bonding situation of this complex cannot be described by the known “boryl” (pure boron donor) or “borane” (pure boron acceptor) descriptions but rather by an unprecedented delocalized Mn-B-Au bonding [4].

- [1] See, e.g.: H. Braunschweig, C. Kollann, D. Rais, *Angew. Chem. Int. Ed.* **2006**, *45*, 5254-5274.
- [2] Y. Segawa, M. Yamashita, K. Nozaki, *Angew. Chem. Int. Ed.* **2007**, *46*, 6710-6713.
- [3] S. Bontemps, G. Bouhadir, K. Miqueu, D. Bourissou, *J. Am. Chem. Soc.* **2006**, *128*, 12056-12057.
- [4] H. Braunschweig, P. Brenner, R. D. Dewhurst, M. Kaupp, R. Müller, S. Östreicher, *Angew. Chem.*, in press.

# Potential energy surface of C<sub>4</sub>H<sub>4</sub>

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Cyclobutadiene (CBD) with its extreme geometry and high reactivity has been subject to numerous experimental and theoretical researches as well as some of its isomers. Reactions that occur on the PES of C<sub>4</sub>H<sub>4</sub> are important in comprehending the combustion and processes occurring in the atmosphere of stars. It is possible that one of the C<sub>4</sub>H<sub>4</sub> compounds could be predecessor to a ring forming process, which could be a key to formations of amino acids. For years NASA has investigated earth-like celestial bodies. In recent years Cassini mission has provided new data about the atmosphere of Saturn's largest moon Titan. It appears that it mainly contains nitrogen and different small hydrocarbons. This in turn has increased interest to PES of CBD and azetes (CHN<sub>3</sub>, C<sub>2</sub>H<sub>2</sub>N<sub>2</sub>, C<sub>3</sub>H<sub>3</sub>N and N<sub>4</sub>). There are those who believe that studying Titan's atmosphere might help to understand processes that occurred on young Earth and even shed some light to the origin of life. PES of C<sub>4</sub>H<sub>4</sub> has been earlier studied by several groups [1-4]. The most thorough research on this PES is by Cremer et al who located 43 minima (including many van der Waals complexes and radicals), using B3LYP, MP2, CCSD(T) and CASSCF level of theory. Cremer et al conclude that most of the carbenes are thermodynamically stable and few of them show also kinetic stability.[4] The aim of this research is to upgrade the data already published on the subject and to shed some light on the combustion pathways of CBD as well as some of its isomers. In our research we omit radicals and excited states that are discussed elsewhere and we concentrate merely on investigating the singlet ground state PES of C<sub>4</sub>H<sub>4</sub>, using density functional theory (DFT) and second order Møller-Plesset perturbation theory (MP2). Although the system studied is very simple the PES of C<sub>4</sub>H<sub>4</sub> is very complicated: with DFT and MP2 we found altogether 35 different minima.

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# Electric and spectroscopic properties of low-lying excited states of acetone

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Present work is aimed on calculations of electric and spectroscopic properties of the ground state and especially low-lying excited states of acetone.

Active space for the ground state consisted of  $\sigma$ ,  $\sigma^*$ ,  $\pi$ ,  $\pi^*$ ,  $n$  and virtual  $n$  orbitals. And for the sake of virtual space consistency another  $\pi^*$  orbital was added into the active space for excited states. Every attempt to use smaller active space ended up with inconsistent results when symmetry was breaking and/or the electric field was applied.

Geometry optimization was performed using CASPT2 method and aug-cc-pVTZ basis set. Molecule is undergoing significant change in geometry during the excitation. CO bond increases its length of about 0.13 Å as a result of excitation from non-bonding to anti-bonding orbital, thus lowering the bond order. Oxygen atom leans out of the CCC plane to form an angle of about 40°.

In the next step vertical (CASPT2/aug-cc-pVQZ:  $^1n-\pi^*$  4,57 eV,  $^3n-\pi^*$  4,26 eV) and adiabatic excitation energies (CASPT2/aug-cc-pVQZ:  $^1n-\pi^*$  3,86 eV,  $^3n-\pi^*$  3,63 eV) were computed. Results converged quickly with the basis set size and were satisfying even within aug-cc-pVDZ basis set.

To determine the electric properties the Finite-Field approach was used. 3, 5, 7, and 9-points central differentiation formulae with equidistant steps of order of 0.001 a.u., 0.002 a.u., and 0.005 a.u. gave us enough results to be able to enumerate the accuracy of the resulting value by means of an interval to which all the results belong.

First four derivatives of energy according to all three coordinates (i.e. the dipole moment, polarizability, and the first two hyperpolarizabilities) and first two derivatives of the expectation values of the dipole moment were determined. The latter allowed us to obtain some of the off-diagonal terms of the electric properties tensors. However, higher derivatives weren't numerically stable. Expectation values of the CASPT2 method are just shifted CASSCF expectation values, as a consequence of invalidity of the Hellmann-Feynman theorem, and are of no use. Energy differentiation results can be compared from both methods and it could be seen that the inclusion of dynamic electron correlation increases in general all resulting

values. This is caused by higher diffuseness of the electron cloud if continuous excitations are allowed. The results obtained with aug-cc-pVDZ and aug-cc-pVTZ basis sets were very close to each other, i.e. the energy was converged in terms of the basis set size.

Dipole momenta were computed with high accuracy ( $10^{-5}$  a.u.). The dipole moment decreases during the excitation almost to half of the value for the ground state (CASPT2/aug-cc-pVTZ: ground state 1.159 a.u.,  $^1n-\pi^*$  0.706 a.u.,  $^3n-\pi^*$  0.643 a.u.). This can be explained by charge transfer towards the center of molecule when the electron originally localized mostly on oxygen atom moves to the orbital localized on the CO bond. Another reason for the decrease is the geometrical factor, as the molecule is more compact after the excitation.

Mean dipole polarizabilities were not affected by the excitation (CASPT2/aug-cc-pVTZ: ground state 41.66 a.u.,  $^1n-\pi^*$  43.50 a.u.,  $^3n-\pi^*$  43.31 a.u.), but their anisotropies decreased by the factor of two (CASPT2/aug-cc-pVTZ: ground state 24.17 a.u.,  $^1n-\pi^*$  11.10 a.u.,  $^3n-\pi^*$  10.78 a.u.). This can be explained by the rough correlation between polarization and the volume of the molecule. While the overall volume does not change during the excitation, change in the shape of molecule means its individual dimensions are changed and this correlates with the changes in polarizabilities in those directions, which tend to be more equal as the molecule gets more compact.

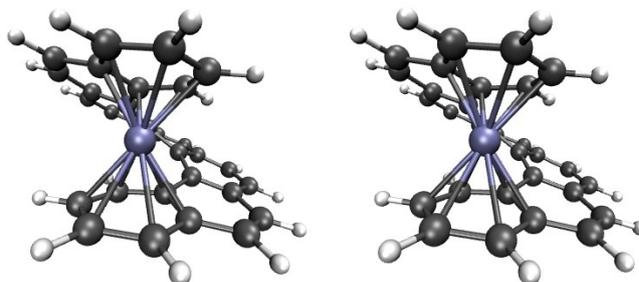
Mean hyperpolarisabilities  $\beta$  were determined with lower accuracy (CASSCF/aug-cc-pVTZ: ground state  $-22.86 \pm 0.5$  a.u.,  $^1n-\pi^*$   $-40.2 \pm 10$  a.u.,  $^3n-\pi^*$   $-50.5 \pm 5$  a.u.).

# Fixing the chirality and trapping the transition state of helicene with atomic metal glue<sup>1</sup>

Michael Patzschke, Mikael P. Johansson

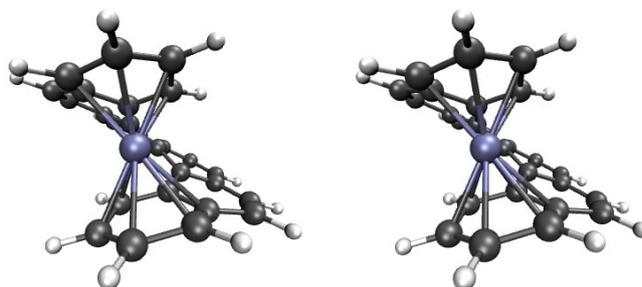
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By combining the intriguing geometrical properties of two classes of well-established molecules, the metallocenes and the helicenes, we propose a hybrid class of structures: the metallohelices. In these, the outermost aryl groups of a specific helicene are glued together by a complexing metal atom. This effectively fixes the chirality of the parent helicene, which otherwise easily undergoes thermal racemization. The fixed chirality suggests several interesting applications, ranging from building blocks of stable molecules with high circular dichroism and optical activity to chiral ligands and catalysts. Alternatively, the metal glue can trap the non-chiral transition state structure of helicene.



Picture 1: Cross-eye stereo picture of W-heptahelicene

A performance study of the meta-GGA TPSS was performed and it was found to perform excellently for bis-benzene metal complexes. We then proceeded to calculate the stability of metallo-helicenes (hexa and heptahelicene) in the geometrical ground state of the helicene for Cr, Mo, W and Pt. These complexes were found to be stable and should readily form. The possibility for a metal to bond to two helicene molecules, thus creating dimer complexes, was also investigated. We furthermore studied the structure and complexation energies for the transition state of the thermal racemisation of hexa- and heptahelicene. These complexes are, as expected, less stable. The energy differences are small enough to make them synthetically viable though.



Picture 2: Cross-eye stereo picture of W-hexahelicene

The studied metallohelices show interesting properties. The helicenes are rather stable, therefore the Fischer-Hafner reduction originally used to prepare bis-benzene chromium might be usable to prepare the metal complexes of helicenes.

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# Computational vibrational spectroscopy of the water nitric oxide complex

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Nitric oxide (NO) is a stable radical molecule that plays a role in various contexts, such as in stratospheric chemistry and in various physiological functions. Hence, the interaction between NO and water is of interest.

The vibrational spectrum of the complex between H<sub>2</sub>O and NO has been studied computationally. The complex is assumed to belong to the  $C_s$  symmetry point group. The calculations have been performed around four minimum energy structures that correspond to the two lowest lying minima of  $A'$  and  $A''$  symmetries. All *ab initio* calculations have been carried out using restricted Hartree-Fock - unrestricted coupled cluster with single, double and perturbative triple excitations method [RHF-UCCSD(T)]. We have used a composite basis set. For the hydrogen atoms, we use the correlation consistent polarized valence quadruple- $\zeta$  (cc-pVQZ) basis, and augment it with diffuse functions for the heavier atoms (aug-cc-pVQZ). The vibrational problem is solved using a model that separates the vibrations of H<sub>2</sub>O and NO. Our kinetic energy operators of the monomer units are exact within the Born-Oppenheimer approximation. We obtain the potential energy operators by calculating a potential energy grid around the minimum energy structure and fitting it to an analytical function. The resulting Schrödinger equation is solved using the variational method. We obtain infrared absorption intensities using a dipole moment function, which is computed using finite differences. Finally, the calculated results are compared to matrix isolation infrared spectra. Similar approach has been successfully used for the water dimer [1].

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## **Localized quantum-chemical descriptors for structure/property predictions**

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This study explains how usage of localized quantum-chemical descriptors can improve molecule activity predictions. Used molecule orbital data from theoretical calculations at different levels: MP2, DFT, Semi-empirical AM1 and PM3. OH radical reaction rate was used as experimental property. Occupied orbital preferably located on active places show good ability to predict electron transfer processes. OH radical reaction with selected organics results in hydrogen abstraction and the most active electron transfer. The last one is very well described by molecule HOMO (highest occupied molecular orbital) energy. The ability of the new descriptors was tested by replacing HOMO (highest occupied molecular orbital) characteristics with localized OMO (localized occupied molecular orbital) ones. In order to develop structure/property relationships for specific mechanisms of action localized descriptors should be used. This approach gives also the relationships more physical sense.

# Redox-coupled proton transfer in the active site of cytochrome *cbb*<sub>3</sub>

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## Abstract

Cytochrome *cbb*<sub>3</sub> is a member of the heme-copper oxidase superfamily, responsible for driving the respiratory chain in many pathogenic bacteria. In analogy to its eukaryotic counterparts, cytochrome *cbb*<sub>3</sub> reduces oxygen to water, and couples the released energy to pump protons across the bacterial membrane. As high resolution crystallographic structures of cytochrome *cbb*<sub>3</sub> oxidases are still lacking, the mechanism of the enzyme has remained elusive. Based on homology modeling and recent Electron Paramagnetic Resonance (EPR) studies on the wild type and a mutant enzyme [V. Rauhamäki *et al.* J. Biol. Chem. 284, 11301-11308, 2009.], we present here results obtained from high-level quantum chemical calculations on the active site of cytochrome *cbb*<sub>3</sub>. Our calculations explain the experimental EPR signals, and indicate that the catalytic mechanism of the enzyme involves a redox-coupled proton transfer between the proximal histidine of the active site heme and a conserved glutamate residue.

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# **Electron Affinity of the O<sub>2</sub> Molecule: CCSD(T) Calculations Using the Optimized Virtual Orbitals Space Approach**

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The electron affinity (EA) of the oxygen molecule is calculated by the CCSD(T) method using the optimized virtual orbitals space (OVOS) technique by which the dimension of the original space of virtual orbitals can be significantly reduced. Extended basis sets, up to the doubly augmented correlation consistent d-aug-cc-pV6Z basis sets for O<sub>2</sub> and O<sub>2</sub><sup>-</sup> at their experimental geometries are used.

We demonstrate that even when the space of virtual orbitals is reduced to 50% of the full space, the resulting EA of the O<sub>2</sub> molecule is accurate to within 0.01 eV. At the same time, the computational effort is reduced by about an order of magnitude. With OVOS reduced to 60% of the full virtual space, results are almost accurate. Considering the complete basis set limit with so reduced OVOS, corrections for the core correlation, vibrational and relativistic effects, the electron affinity of O<sub>2</sub> is 0.452 ± 0.01 eV. This value agrees very well with the full virtual orbital space, EA = 0.446 eV, and with the recent experimental value, EA = 0.448 ± 0.006 eV.

# **Variational calculations of the stretching and bending modes of an ammonia molecule adsorbed on metal surfaces**

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The vibrational frequencies of a molecule shift when it adsorbs on a surface. In order to understand the origin of this shift better, we have computationally modeled the vibrational motion of an isolated ammonia molecule and ammonia molecules adsorbed on Cu(111), Ni(111) and Pt(111) surfaces using the same computational method. The exact kinetic energy operator for an isolated ammonia has been combined with the vibrational potential energy surfaces that have been obtained from plane-wave based density functional theory calculations. The resulting Hamiltonian has been solved variationally.

# Magnetically induced currents in bianthraquinodimethane-stabilized Möbius and Hückel [16]annulenes

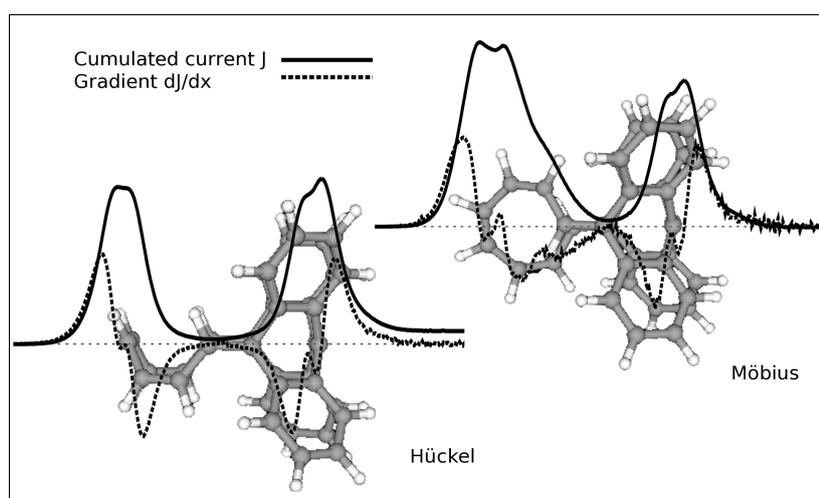
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The aromaticity of bianthraquinodimethane-stabilized [16]annulenes possessing Hückel and Möbius topology has been discussed in the literature [1,2]. The Möbius isomer was the first cyclic hydrocarbon with  $4n$  electrons possessing Möbius topology to be synthesized [1]. To shed light upon the question about the aromaticity of this molecule, its Möbius and Hückel isomers have been investigated [3] by calculating the magnetically induced current density using the Gauge-Including Magnetically Induced Current (GIMIC) approach [4].

Numerical integration of the current density circling around the [16]annulene ring shows that both the Hückel and the Möbius isomers are nonaromatic. The [16]annulene ring of both isomers sustains a net ring current whose strength is only 0.3 nA/T. The ring current consists of a diamagnetic flow on the outside of the [16]annulene ring and a paramagnetic current inside it. Since the net ring-current strength of the [16]annulene in the studied molecule is less than 5% of the ring current for benzene, both isomers must be considered nonaromatic. The shape of the ring-current of the Möbius isomer shows that the current density is somewhat more outspread than for the Hückel isomer. Spatially separated diatropic and paratropic currents of equal strength follow the annulene bonds. In spite of the slightly different current profiles, the  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR chemical shifts are rather similar for the two isomers.



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# The role of d-orbital in hypervalency molecule

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The concept 'hypervalency' was proposed for main-group elements exceeding formal eight electron sharing, e.g. SF<sub>6</sub>. [1] The traditional explanation involving sp<sup>3</sup>d<sup>n</sup> hybridization. This mechanism is challenged and almost abandoned now. [2–5] The role of d-orbital is nevertheless still under discussion, including (a) not important [6] (b) polarization function [7] (c) correlation function [8] (d) electron back-donation from fluorine to sulphur [3].

We start from the canonical molecular orbital, for SF<sub>6</sub> with *O<sub>h</sub>* point-group symmetry. The d-orbital of sulphur spans *e<sub>g</sub>* and *t<sub>2g</sub>* irreducible representations. The orbital picture and Morokuma energy decomposition suggest the d-orbital provide an important energetic contribution *c.a.* - 400 kJ mol<sup>-1</sup>.

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# Electronic Structure of Jahn-Teller Active Molecules

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The Jahn-Teller theorem [1, 2] states that in a molecule with a degenerate electronic state, a structural distortion must occur that lowers the symmetry, removes the degeneracy and lowers the energy. The detailed analysis of latter is a challenge due to the superposition of effects produced by many different vibrational modes. Inspection of the path of minimal energy from the HS nuclear configuration towards the LS energy minimum, Intrinsic Distortion Path (IDP) [3] gives the detailed information on the vibronic coupling. Bonding analysis can be useful in rationalizing which normal modes are the most adequate for the energy stabilization due to the distortion.

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