



Orbital-Dependent Density Functionals for Catalysis

Pd interactions with polyenes in complexes

Boris B. Averkiev, Yan Zhao, and Donald G. Truhlar, University of Minnesota

Palladium interactions with alkenes and conjugated π systems are very important in a number of catalytic contexts. In 2010, the Nobel Prize in Chemistry was awarded to Richard Heck, Ei-ichi Negishi, and Akira Suzuki for their work in designing palladium catalysts. A key part of rational catalyst design is understanding the effect of ligands, and quantum chemical methods can be very helpful for this. However, most catalytic systems are too large to be modeled by wave function theory. Such systems can be treated by density functional theory (DFT) due to its high performance/cost ratio. Although DFT has been very useful for understanding and predicting transition metal chemistry, it was reported by Sakaki and coworkers that DFT significantly underestimates the binding energies of d^{10} centers of Pd to ethene and conjugated π systems with 2 to 5 double bonds, with the errors increasing in magnitude as the ligand becomes larger.

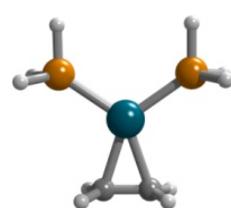
In recent years, our group has developed several density functionals with broad applicability, and we have now applied them to olefin binding to Pd centers. Our results show that our recently developed density functionals predict the binding energy for these systems much more accurately than the functionals tested by Sakaki. New benchmark calculations carried out with the coupled cluster method based on Bruecker orbitals with double excitations and a quasiperturbative treatment of connected triple excitations (BCCD(T)) with a very large basis set and explicitly correlated coupled cluster method with single and double excitations and a quasiperturbative treatment (CCSD(T)-F12) agree even better with the DFT predictions than do the previous best estimates. The best mean unsigned errors for DFT are only 1.3 and 1.5 kcal/mol for the M06-D and M06-L-D functionals, respectively.

All DFT calculations were carried out with *Gaussian 09* program.

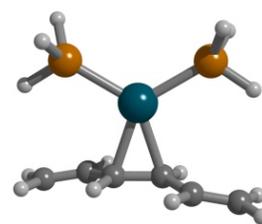
All CCSD(T) and BCCD(T) calculations were carried out with MOLPRO 2009 program.

Binding Energy of Transition-Metal Complexes with Large π -Conjugate Systems. Density Functional Theory vs Post-Hartree-Fock Methods, A. Ikeda, Y. Nakao, H. Sato, and S. Sakaki, *J. Phys. Chem. A* **111** 7124–7132 (2007).

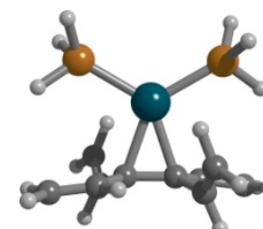
Binding Energy of d^{10} Transition Metals to Alkenes by Wave Function Theory and Density Functional Theory, B. B. Averkiev, Y. Zhao, and Donald G. Truhlar, *J. Mol. Cat. A-Chem.* **324**, 80-88 (2010).



$\text{Pd}(\text{PH}_3)_2\text{C}_2\text{H}_4$
 $n = 2$

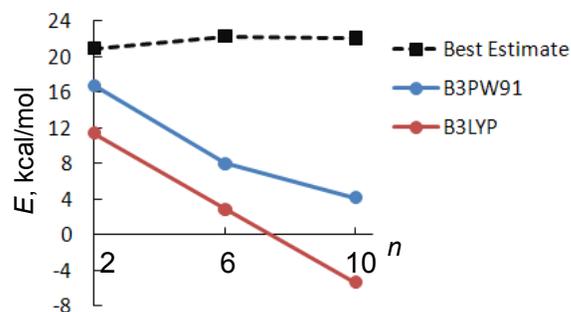


$\text{Pd}(\text{PH}_3)_2\text{C}_6\text{H}_8$
 $n = 6$

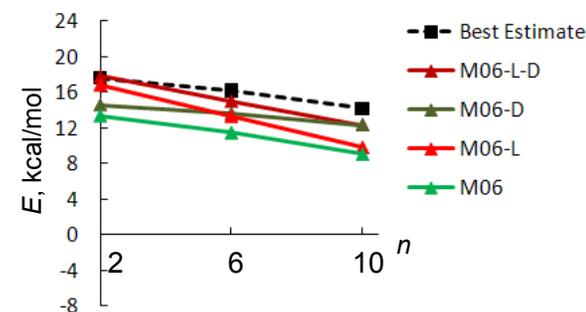


$\text{Pd}(\text{PH}_3)_2\text{C}_{10}\text{H}_{12}$
 $n = 10$

Sakaki results



Our results



	B3PW91	B3LYP	BLYP	BP86	PBE0	B98	B97-1	B98-2	M06	M06-L	M06-L-D	M06-L-D
MUD	7.2	9.5	10.7	6.5	5.1	7.1	6.5	8.3	2.5	2.9	1.3	1.5

MUD denotes mean unsigned deviation from the best estimate for ten quantities, namely four absolute binding energies ($n = 2, 6$, and two isomers for 10) and six relative binding energies (pairwise comparisons of the four structures).