CLAMSHELL STRUCTURES OF HAFNIUM AND ZIRCONIUM BIPHENYL COMPLEXES DETERMINED BY PULSED FIELD IONIZATION ELECTRON SPECTROSCOPY

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Biphenyl, $C_{12}H_{10}$, has a planar structure in the crystalline state and is twisted in the gas phase. Previously, our group discovered that Sc and Ti coordination induced phenyl ring rotation and bending.[a,b] In this work, we extended the study of metal-biphenyl complexes to heavy transition elements. Zr- and Hf-biphenyl complexes were produced in a laser ablation molecular beam source and studied by pulsed field ionization-zero electron kinetic energy (ZEKE) photoelectron spectroscopy. Like Sc and Ti, the Hf and Zr complexes prefer clamshell structures and low electron spin states. The clamshell structures are formed by metal binding to both phenyl rings and have C_{2v} symmetry. The ground electronic states of both complexes are $^1A_1$ in the neutral form and $^2B_1$ in the ionized form. The ionization energies were measured to be 43341(5) and 43750(5) cm^{-1} for the Zr- and Hf-biphenyl complexes, respectively. In addition, a number of metal-phenyl and phenyl-based vibrations were observed for the neutral and ionic states of the two complexes.

[a] B. R. Sohnlein, J. F. Fuller, and D. S. Yang, J. Am. Chem. Soc. 128 (33), 10692 (2006).
[b] B. R. Sohnlein, Ph.D. Dissertation, University of Kentucky, July 2007.