

## Bonding in 5-Membered Cyclic Alkynes: Charge Density in 1-Zirconacyclopent-3-yne

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Small cyclic alkynes are, in general, unstable because of ring strain. Recently, 1-zirconacyclopent-3-yne complexes, viz 5-membered cyclic alkynes, were synthesized.[1] The bonding nature of the complexes has been investigated by theoretical calculations[2], but is still in controversy. Here we show the bonding nature of the 1-zirconacyclopent-3-yne complex by means of experimental charge density analysis.

Diffraction data were collected using synchrotron radiations at KEK PF-AR NW2 beam line by Rigaku Mercury CCD diffractometer up to  $\sin\theta/\lambda = 1.0 \text{ \AA}^{-1}$ . Multipole expansion method was applied for modeling of atoms. Final  $R$  was 0.027 for reflections with  $I > 1.5\sigma(I)$ .

The 1-zirconacyclopent-3-yne moiety is planar. Valence shell charge concentrating region on each of the C atoms on the  $\alpha$  positions extends toward the charge depressing regions on the Zr atom. Bond critical points and bond paths were found on the Zr-C( $\alpha$ ) bonds. The bond paths curve inwardly near the C( $\alpha$ ) atoms. These suggest that both of the  $\eta^2$ - $\sigma$ ,  $\sigma$  and  $\eta^4$ - $\pi$ ,  $\pi$  structures contribute to the bonding. No bond paths, in contrast, were found on the Zr-C( $\beta$ ) bonds. In conclusion, bonding of 1-zirconacyclopent-3-yne is in resonance between  $\eta^2$ - $\sigma$ ,  $\sigma$  and  $\eta^4$ - $\pi$ ,  $\pi$  structures.

[1] a) Suzuki N. *et al.*, *Science*, 2002, **295**, 660; b) Suzuki N. *et al.*, *J. Am. Chem. Soc.*, 2004, **126**, 60. [2] a) Lam K. C., Lin, Z., *Organometallics*, 2003, **22**, 3466; b) Jemmis E. D. *et al.*, *Organometallics*, 2003, **22**, 4958.

**Keywords:** charge density, chemical bonding, zirconium compounds