

# Theoretical Study on Internal Alkyne/Vinylidene Isomerization on Group 8 Transition Metal Complexes

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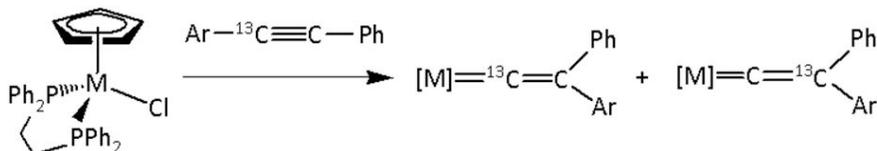
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Alkyne/vinylidene isomerization in transition metal complexes has been exploited in the synthesis of a wide range of vinylidenes. Recently, Ishii and his co-workers reported the internal alkyne/vinylidene isomerization of  $[\text{CpM}(\text{PhC}\equiv\text{CC}_6\text{H}_4\text{R}-p)(\text{dppe})]^+$  ( $\text{M} = \text{Fe}, \text{Ru}$ ;  $\text{R} = \text{OMe}, \text{Me}, \text{H}, \text{Cl}, \text{and CO}_2\text{Et}$ ) [1,2], and our DFT study on the Ru complexes clarified that the migration reaction is nucleophilic[3]. However, effects of the central metal on the reaction remain unrevealed. Herein, we report the results of DFT calculations on the transformation of internal alkyne complexes having group 8 transition metals,  $[\text{CpM}(\text{PhC}\equiv\text{CC}_6\text{H}_4\text{R}-p)(\text{dppe})]^+$  ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ;  $\text{R} = \text{OMe}, \text{CO}_2\text{Et}, \text{and Cl}$ ), and discuss the metal effects on the reaction.



Geometry optimization followed by frequency calculations and intrinsic reaction coordinate (IRC) calculations were performed with the B3PW91 functional. The ECP and basis set used are SDD for the metals and 6-31G(d) for the remaining nonmetal atoms. The combined basis set is denoted by SDD+6-31G(d) in the present study. NBO analysis was carried out at the HF level of theory.

Two types of 1,2-migration pathway were obtained for each metal complex, which are paths 1 and 2 in the Fe complex and paths 1 and 3 in the Ru and Os complexes. The activation free energies for paths 2 and 3 were smaller than that for path 1, respectively. Thus, the isomerization reaction of internal alkynes to vinylidenes proceeds through paths 2 and 3. The difference between path 2 (Fe complex) and path 3 (Ru and Os complexes) is in geometry of the reactants. The difference in the reactant structures is due to the different characteristics of the valence d orbitals of Fe in the complex from those of the other metals, which lead to different types of overlap between the d orbitals of the metal and the  $\pi$  orbital of the alkyne. To assess the stability of alkyne and vinylidene complexes for three kinds of metals, orbital interaction energies between the alkyne/vinylidene moiety and the other parts of organometallic complex were calculated by NBO analysis. It was revealed that the Os complex has the strongest interaction for both cases, followed by the Ru and Fe complexes.

[1] Y. Mutoh *et al.*, *Chem. Lett.*, **2009**, 38, 534. [2] Y. Mutoh *et al.*, *Organometallics*, **2011**, 30, 204.

[3] M. Otsuka *et al.*, *J. Am. Chem. Soc.*, **2012**, 134, 17746.