Conformational transformations in ruthenocene and osmocene coupled to the CH···Ru and CH···Os bonds

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So far, ferrocene ($FeCp_2$) was the only known metallocene crystal, undergoing transformations coupled with a change of molecular conformation. [1] Other metallocenes are either disordered in the staggered conformation or ordered in the eclipsed conformation. The 18-electron metallocene complexes, chemically stable, ferrocene, ruthenocene ($RuCp_2$) and osmocene ($OsCp_2$) occur in orthorhombic crystalline space group *Pnma* ($RuCp_2$ and $OsCp_2$ at ambient condition, while $FeCp_2$in its low-temperature phase III). [1] Till recently, ruthenocene and osmocene were studied at ambient and low temperature and they have been known in the isostructural phases α only.

Under high-pressure conditions, we obtained the β phases of $RuCp_2$ [2] and $OsCp_2$ [3]. In these new phases, the CH···*M* bonds (*M*=Ru, Os) become significant. The calculation of the electrostatic potential on the $FeCp_2$, $RuCp_2$ and $OsCp_2$ molecules' surface revealed that $OsCp_2$ has the highest affinity to form CH···*M* bonds, while that of $FeCp_2$ is the lowest. Structural analysis confirmed these theoretical results: for each $OsCp_2$ molecule in phase β, there are 4 independent CH···*M* contacts, while for each $RuCp_2$ molecule in β phase, there is only 1 independent CH···*M* contact.

Our latest high-temperature diffraction experiments on single crystals revealed isostructural γ phases of $RuCp_2$ (T_c= 394 K) and $OsCp_2$ (T_c= 422 K). Each carbon atom in the Cp ring in those γ phases is disordered in four sites, two due to the seesaw movement of molecules about the [*y*] axis and another two due to the Cp rings rotation about the pseudo-C_5 molecular axis (Figure 1). The mechanism of the phase transition is connected with the breaking of CH···*M* contacts, which are present in the α and β phases of $RuCp_2$ and $OsCp_2$.

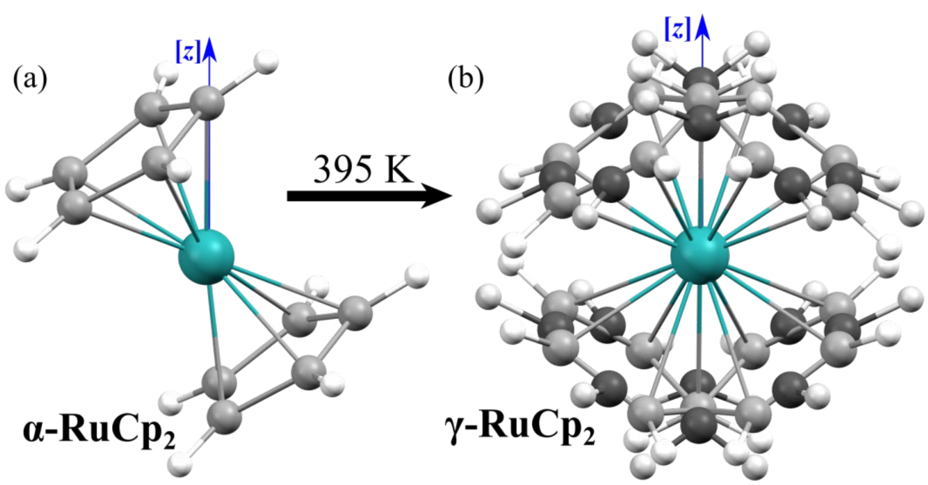

Figure 1. Ruthenocene molecule in (a) ordered phase α at 296(2) K and (b) disordered phase γ at 395(2) K.

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