

## MS27-2-5 High-Pressure Polymorphs of Osmocene and Ruthenocene #MS27-2-5

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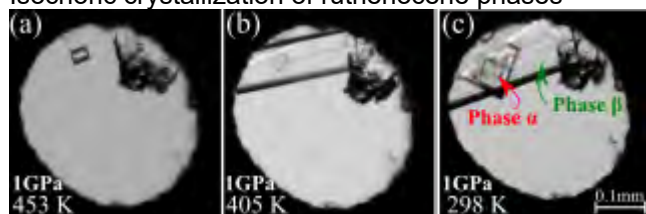
### Abstract

Ruthenocene ( $\text{RuCp}_2$ )<sup>1</sup> and osmocene ( $\text{OsCp}_2$ )<sup>2</sup> are isostructural, at ambient conditions they both crystallize in the orthorhombic space group  $Pnma$ . However, high pressure conditions reveal phase transitions to two different polymorphs, space groups  $Pcmb$  at 3.9 GPa<sup>3</sup> and  $Pcab$  at 3.5 GPa for  $\text{RuCp}_2$  and  $\text{OsCp}_2$  respectively. In both cases there is a large pressure hysteresis (about 3.15 GPa) in which  $\alpha$  and  $\beta$  phases can coexist (Figure 1).  $\alpha$ -phases of both compounds are mostly stabilized by C-H $\cdots\pi$  contacts. High-pressure phase transformations occur because of competitive impact of C-H $\cdots\pi$  and C-H $\cdots$ M contacts. Non-identical way of high pressure transitions of these two compounds arises from different preference to create anagostic M $\cdots$ H-C interactions. In  $\beta$ - $\text{OsCp}_2$  there are 4 different anagostic contacts, while in  $\beta$ - $\text{RuCp}_2$  only one H $\cdots$ M distance is shorter than the sum of van der Waals radii (Figure 2). The arrangement of short contacts around osmium cation in  $\beta$ - $\text{OsCp}_2$  leads to eliminate mirror plane symmetry in the crystal structure. In  $\beta$ -osmocene the shortest Os $\cdots$ H contact is longer than the shortest Ru $\cdots$ H contact in  $\beta$ -ruthenocene. All phase transitions of metallocenes published already in the literature involve changes in molecular conformations, which differ from transformation of  $\text{RuCp}_2$  and  $\text{OsCp}_2$ .

### References

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2. Bobyens, J. C. A.; Leventis, D. C.; Bruce, M. I.; Williams, M. L. Crystal Structure of Osmocene,  $\text{Os}(\eta\text{-C}_5\text{H}_5)_2$ . *J. Crystallogr. Spectrosc. Res.* 1986, 16 (4), 519–524. DOI: 10.1007/BF01161040.
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### Isochoric crystallization of ruthenocene phases



### Anagostic M-H contacts in ruthenocene and osmocene

