Ruthenocene (RuCp₂)¹ and osmocene (OsCp₂)² 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 Pcmn at 3.9 GPa³ and Pcab at 3.5 GPa for RuCp₂ and OsCp₂ respectively. In both cases there is a large pressure hysteresis (about 3.15 GPa) in which α and β phases can coexist (Figure 1). α-phases of both compounds are mostly stabilized by C-H···π contacts. High-pressure phase transformations occur because of competitive impact of C-H···π and C-H···M contacts. Non-identical way of high pressure transitions of these two compounds arises from different preference to create anagostic M···H-C interactions. In β-OsCp₂ there are 4 different anagostic contacts, while in β-RuCp₂ only one H···Ru distance is shorter than the sum of van der Waals radii (Figure 2). The arrangement of short contacts around osmium cation in β-OsCp₂ leads to eliminate mirror plane symmetry in the crystal structure. In β-osmocene the shortest Os···H contact is longer than the shortest Ru···H contact in β-ruthenocene. All phase transitions of metallocenes published already in the literature involve changes in molecular conformations, which differ from transformation of RuCp₂ and OsCp₂.

References

Isocoric crystallization of ruthenocene phases

Anagostic M-H contacts in ruthenocene and osmocene