

Greenwood & Earnshaw

2nd Edition

Chapter 21

Group 4

**Titanium, Zirconium &
Hafnium**

Halides of Ti, Zr, Hf

TiF₄ – Non-volatile, mp 284 °C, octahedral Ti, bridging Fluorine.

TiX₄ – X = Cl, Br, I, Volatile, tetrahedral molecules, colors varying from colorless – orange – dark brown due to a charge transfer band moving further into the visible induced by the highly polarizing Ti(IV) effect on the more easily oxidized heavier halogen anions.

Compound	Color	MP/°C	BP/°C
TiF₄	white	284 °C	---
TiCl₄	colorless	-24 °C	136.5 °C
TiBr₄	orange	38 °C	233.5 °C
TiI₄	dark brown	155 °C	377 °C

ZrF₄ – 8 CN M, sq. antiprismatic, non-volatile.

ZrX₄ – X = Cl, Br, I, Volatile, 6CN, O_h zig-zag polymer chains.

Organometallics of Ti, Zr, Hf

Binary Carbonyls: $\text{Ti}(\text{CO})_6$ - stable at low temperature, little M- π^* back-bonding. In contrast, the $[\text{Ti}(\text{CO})_6]^{2-}$ and $[\text{Zr}(\text{CO})_6]^{2-}$ complexes are exceptionally thermally stable to 200°C . π -Donor ligands such as cyclopentadiene stabilize mixed carbonyls.

Alkyls: β -elimination of hydrogen occurs easily. Carbene or alkylidene complexes are stable, very important in catalysis, cf Ziegler-Natta catalysis.

Cyclopentadienyl Complexes are stable and provide the majority of the organometallic chemistry of this group. The $\text{Ti}(\text{Cp})_2\text{X}_2$ compounds are stable to air and have an extensive aqueous chemistry. Subtle rearrangements, fluxionality and unusual coordination hapticities occur as well as changes down the group.