

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
TiF ₄	white	284°C	---
TiCl ₄	colorless	-24°C	136.5°C
TiBr ₄	orange	38°C	233.5°C
TiI ₄	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: Ti(CO)₆ - stable at low temperature, little M- π^* back-bonding. In contrast, the [Ti(CO)₆]²⁻ and [Zr(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 Ti(Cp)₂X₂ 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.
