Greenwood & Earnshaw

2nd Edition

Chapter 29

Group 12

Zinc, Cadmium, Mercury

Zinc, Cadmium, Mercury

•Oxidation states limited to +1 (Hg) and +2. First and second IE lower than preceding group, 3rd IE larger, stable d^{10}.

• Electronegativities rise going down group, but large jump not apparent, lower than preceding group: Zn < Cu; Cd < Ag; Hg < Au

•Mp & bp are much lower that preceeding group, Hg at –38.9 C is the lowest mp of any metal.

• ΔH_{vap} is lower than preceding group, Hg = 61.3 kJ/mol and is monatomic in the gas phase, $P_{vap} = 1.9 \times 10^{-3}$ torr at 25°C.

Zinc, Cadmium, Mercury

- **Zn (76 ppm), Cd (0.16 ppm, Hg (0.08 ppm) are not rare.**
- **Zn & Cd are very reactive, tarnish in air, Hg much slower, lanthanide contraction stabilizes and reduces the reactivity of the $6s^2$, also accounts for large rise in electrical resistivity reduced metallic bonding and more modest rise in density.**
- **Zn is biologically one of the most important metals, a fact overlooked due to its wide distribution and low concentration in virtually every cell, adult has ~ 2g Zn.**
- **Cd & Hg are among the most toxic metals biologically.**

Zinc, Cadmium, Mercury

- **Zn - Used in alloys (brass, inexpensive castings), protective coatings (galvanizing), dry cells (Zn, C, MnO_2), medicinally ($ZnO/ZnCO_3$ calamine aids healing). Sulfide ores most common, found w/Pb.**
- **Cd – Used in rechargeable batteries (NiCad), protective coating (plating limited by toxicity, Zn mimic.)**
- **Hg – Amalgamation (precious metals extraction), batteries (Zn/Hg), electronic devices where liquid state important, bacteriacide, fungicide (timerosal in vaccines, uses dying due to cummulative toxicity, sensitivity of young children), UV lamps (street lights).**

Zinc, Cadmium, Mercury - Halides

Table 29.3 Halides of zinc, cadmium and mecury (mp, bp, in parentheses)

Fluorides	Chlorides	Bromides	Iodides
ZnF_2 white (872°, 1500°)	$ZnCl_2$ white (275°, 756°)	$ZnBr_2$ white (394°, 702°)	ZnI_2 white (446°, d > 700°)
CdF_2 white (1049°, 1748°)	$CdCl_2$ white (568°, 980°)	$CdBr_2$ pale yellow (566°, 863°)	CdI_2 white (388°, 787°)
HgF_2 white (d > 645°)	$HgCl_2$ white (280°, 303°)	$HgBr_2$ white (238°, 318°)	HgI_2 α red, β yellow (257°, 351°)
Hg_2F_2 yellow (d > 570°)	Hg_2Cl_2 white (subl 383°)	Hg_2Br_2 White (subl 345°)	Hg_2I_2 yellow (subl 140°)

- **Only Hg has important +1 oxidation state.**
- **All M(II) except fluorides show significant covalency.**
- **ZnX_2, CdX_2, HgF_2, Hg_2F_2 hydrolyze in water or are very hygroscopic.**
- **$ZnCl_{2(aq)}$ conc. dissolves cellulose, many metal oxides.**

Mercury Cations

$$HgCl_2 + 2\,Hg + 2\,AlCl_3 \xrightarrow{\Delta} Hg_3(AlCl_4)_2$$

$$\left[Hg \overset{255\ pm}{\text{——}} Hg \text{——} Hg \right]^{2+}$$

$$\left[Hg \overset{250 - 270\ pm}{\text{——}} Hg \right]^{2+}$$

$$\underset{\text{colorless}}{\left[Hg \text{——} Hg \right]^{2+}} + x\left[AsF_6 \right]^{-}$$

$$n\,Hg + m\,AsF_5 \xrightarrow[SO_{2(l)}]{} \underset{\text{orange}}{\left[Hg \overset{255\ pm}{\text{——}} Hg \text{——} Hg \right]^{2+}} + yAsF_3$$

$$\underset{\text{deep red - black}}{\left[Hg \overset{255\ pm}{\text{——}} Hg \overset{262\ pm}{\text{——}} Hg \overset{259\ pm}{\text{——}} Hg \right]^{2+}}$$

The almost linear cations are extremely moisture sensitive.

Hg_2^{2+} salts which are soluble exist in an easily displaced equilibrium with Hg^{2+} [Hg(II)/Hg(I) = .0061] and disproportionate easily with anions selective for Hg(II).

Zinc, Cadmium, Mercury - Organometallics

Table 29.4 Comparison of some typical organometallic compounds MR_2

R	Zn MP/°C	Zn BP/°C	Cd MP/°C	Cd BP/°C	Hg MP/°C	Hg BP/°C
Me	−29.2	46	−4.5	105.5	—	92.5
Et	−28	117	−21	64 (19 mmHg)	—	159
Ph	107	d 280	173	—	121.8 (subl)	204 (10 mmHg)

$$MX_2 \xrightarrow{RMgX} RMX \xrightarrow{RMgX} R_2M$$

$$M + CH_3I \longrightarrow CH_3MI$$

Cd & Zn alkyls more reactive . than Hg , less reactive than Mg , don't react with CO_2 .

$$2\,CH_3MX \xrightarrow{\Delta} (CH_3)_2M + MX_2$$

$$Hg(Na) + RX \longrightarrow R_2Hg + NaX$$

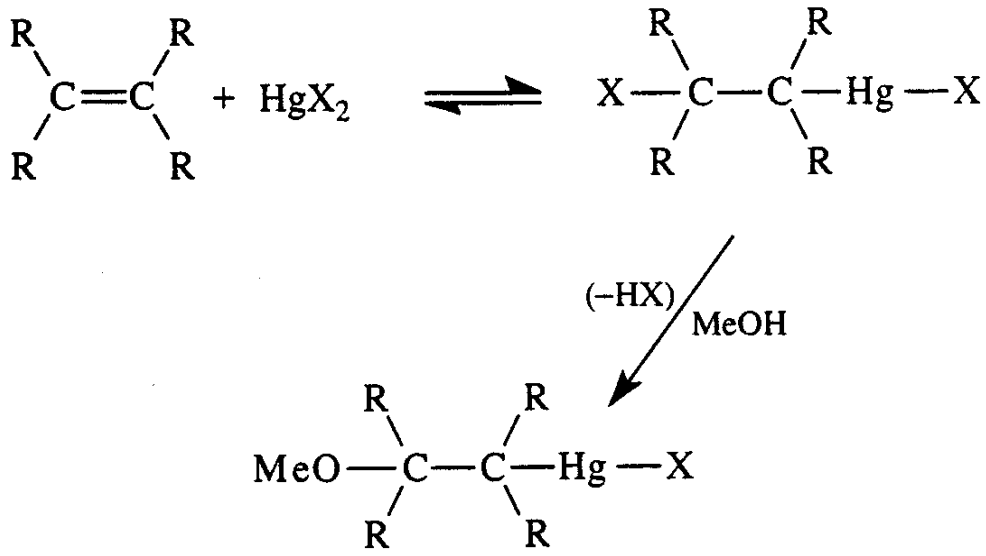
Industrial, X = Br

R_2M & RMX; M = Zn pyrophoric, fume in moist air, Cd less.

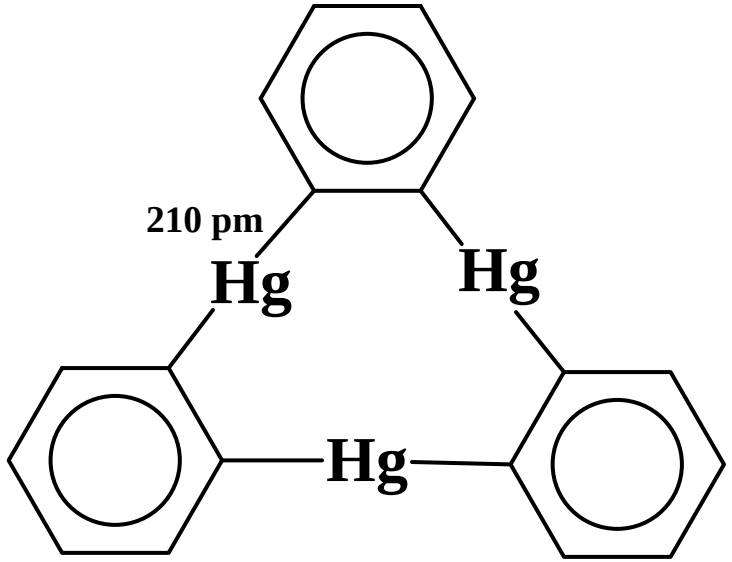
Important trifluoromethylating agents esp w/ CuX

CF_3ZnX $(CF_3)_2Zn$ CF_3CdX $(CF_3)_2Cd$

Mercury - Organometallics

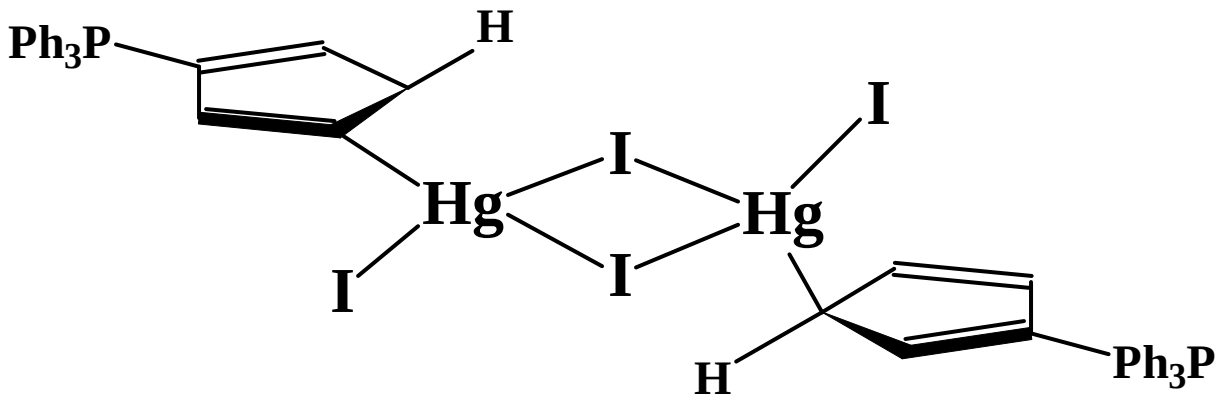


The reluctance of Hg to form pi complexes is well documented. Oxomercuration is an addition reaction to an alkene.



The tendency of all mercury alkyls to attain linear geometry sometimes results in oligomerization.

Mercury - Cyclopentadienyls



One of the few crystal structures of a cyclopentadienyl mercury shows η^1 coordination and an essentially tetrahedral environment about the mercury.

$[Hg(C_5H_5)_2]$

$[Hg(C_5H_5)X]$

The cyclopentadienyls of mercury are photosensitive and difficult to crystallize. NMR and IR data indicate η^1 coordination and fluxional behavior, “ring whizzers”.

Mercury - Toxicity

The toxicity of mercury is associated with mercury's affinity for sulfur. Mercury attacks –S- and –SH linkages principally cysteine residues.

CH_3Hg^+ is particularly dangerous since it can be formed from inorganic mercury deposited in sediments where anaerobic bacteria can act on it. It accumulates in predator fish and can readily cross the intestinal membranes into the blood stream where its immediate effect on the brain and nervous system is severe.

R_2Hg liquid alkyls are particularly dangerous in the laboratory as they easily penetrate even neoprene gloves, pass directly through the skin and into the body.

Unusual Stability of Mercury(0)

- **The Thermodynamic "Inert pair Effect" is complex. Extends to all p-block Sixth Period n-2 oxidation states.**
- **Partly arises from diminishing bond strengths as the oxidation states increase, and the transition to covalent bonding from ionic bonding.**
- **Partly arises from relativistic effects that occur for electrons as Z increases. For a "hydrogen like" atom of Z = 1, v = 1/137 c; for an atom of Z = 80, v = 0.58 c; and the relativistic mass of the electron increases to 1.28 m_0.**
- **Nuclear shielding Δ's cause a contraction in ns AO's, little change in p AO's and an expansion in d AO's.**