

Selections from Chapter 16 Carbonyls, Organometallics, ...

CHEM 462
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T. Hughbanks

18 e “rule” (a guideline, actually)

We now consider the class of T.M. compounds where most of the bound ligands are carbonyls, phosphines, arsines, stibines, NO, bipy, etc...

- ◆ The number of ligand electrons available for bonding plus the number electrons on the metal in such complexes adds to 18.
- ◆ Simple mononuclear carbonyl complexes:

Mononuclear Carbonyls

$\text{V}(\text{CO})_6$	$\text{Cr}(\text{CO})_6$	$\text{Fe}(\text{CO})_5$ yellow liq.	$\text{Ni}(\text{CO})_4$ colorless liquid, b.p. 43 °C
blue-black solid, paramag. ($1e^-$), yellow-orange in solution	$\text{Mo}(\text{CO})_6$	$\text{Ru}(\text{CO})_5$	
	$\text{W}(\text{CO})_6$	$\text{Os}(\text{CO})_5$ colorless liquids	Pd & Pt analogs not stable
	colorless crystals		

Binuclear & Polynuclear Carbonyls

- ◆ $\text{Mn}_2(\text{CO})_{10}$, $\text{Tc}_2(\text{CO})_{10}$, $\text{Re}_2(\text{CO})_{10}$
- ◆ $\text{Co}_2(\text{CO})_8$
- ◆ $\text{Fe}_2(\text{CO})_9$, $\text{Ru}_2(\text{CO})_9$, $\text{Os}_2(\text{CO})_9$ (last two not very stable)
- ◆ $(\text{Fe,Ru,Os})_3(\text{CO})_{12}$
- ◆ $(\text{Co,Rh,Ir})_4(\text{CO})_{12}$
- ◆ Issues: bridging, semibridging, and side-on carbonyls, fluxionality

Vibrational Spectra

- ◆ CO stretching frequencies are important in characterization of carbonyl-containing compounds - relatively intense and sensitive to bonding and charge variations.
- ◆ Free CO: 2170 cm^{-1} ; Some trends (cm^{-1}):
 $\text{Mn}(\text{CO})_6^+$ (2090); $\text{Cr}(\text{CO})_6$ (2000); $\text{V}(\text{CO})_6^-$ (1860)
 $\text{Cr}(\text{dien})(\text{CO})_3$ (1900, 1760)
terminal COs (neutral): $1850\text{--}2125\text{ cm}^{-1}$
bridging COs (neutral): $1700\text{--}1860\text{ cm}^{-1}$

Preparation of Metal Carbonyls

- ◆ Direct Reaction (Ni; Co & Fe at high temp):
 $\text{Ni (finely divided)} + 4\text{ CO (g)} \rightarrow \text{Ni}(\text{CO})_4(\text{g})$ (25°C)
 $\text{Fe (finely divided)} + 5\text{ CO (g)} \rightarrow \text{Fe}(\text{CO})_5(\text{g})$ (200 bar, $> 150^\circ\text{C}$)
- ◆ Most other carbonyl compounds prepared via reduction:
 $\text{MX}_n + \{\text{Na, Al, Mg, R}_3\text{Al, Cu}\} \rightarrow \text{M}(\text{CO})_n + \{\text{NaX, AlX}_3, \text{MgX}_2, \text{CuX}\}$
The course of these reactions is not well-known, may involve reduction to particulate metals
- ◆ Sometimes CO itself is the reducing agent:
$$\text{CoCO}_3 + 2\text{H}_2 + 8\text{CO} \xrightarrow{250\text{--}300\text{ atm, }150^\circ\text{C}} \text{Co}_2(\text{CO})_8 + 2\text{CO}_2 + 2\text{H}_2\text{O}$$

$$\text{Re}_2\text{O}_7 + 17\text{CO} \rightarrow \text{Re}_2(\text{CO})_{10} + 7\text{CO}_2(\text{g}) \quad \sim 300\text{ atm, } \sim 300^\circ\text{C}$$

$$\text{OsO}_4 + 9\text{CO} \rightarrow \text{Os}(\text{CO})_5 + 4\text{CO}_2(\text{g}) \quad \sim 350\text{ atm, } \sim 250^\circ\text{C}$$

CO analogs

♦ Isocyanides (isonitriles): $\text{:C}\equiv\text{N}-\text{R}$

- Stronger σ donor, about as good a π acceptor as CO

Direct analogs, e.g., $\text{Cr}(\text{CNPh})_6$, $\text{Ni}(\text{CNPh})_4$

Since CNR are better σ donors, isocyanide complexes can be made where π -backbonding is less favorable, eg., $[\text{Fe}(\text{CNR})_6]^{2+}$, $[\text{Ag}(\text{CNR})_4]^+$

♦ Dinitrogen : weaker as a σ donor and π acceptor

Complexes can be prepared (under strongly reducing conditions): $\text{MoCl}_5 + 2\text{N}_2 + 4 \text{PR}_3 + \text{Na/Hg} \rightarrow$
 $\text{trans-Mo}(\text{N}_2)(\text{PR}_3)_4 + 5 \text{NaCl}$ (in THF)

Nitrosyls

- ♦ Linear nitrosyls are similar to linear carbonyls, except they are categorized as $3e^-$ donors (if counted as neutral!).

- ♦ NO π -backbonding very strong (stronger than CO)

- ♦ Longest known isoelectronic series of neutrals: $\text{Ni}(\text{CO})_4$, $\text{Co}(\text{CO})_3(\text{NO})$, $\text{Fe}(\text{CO})_2(\text{NO})_2$, $\text{Mn}(\text{CO})(\text{NO})_3$, $\text{Cr}(\text{NO})_4$ (only known pure nitrosyl)

- ♦ bent nitrosyls: neutral called a “one- e^- donor”

Nitrosyls: e^- counting pitfalls

- ♦ An alternative to the odd- e counting assignment: if linear, call it “ NO^+ ”, if bent call it “ NO^- ” - then it is always a $2e^-$ donor.

- ♦ Why bother? Examples

Structure of $\text{Co}(\text{NH}_3)_5(\text{NO})$?

Ox. state and magnetism of $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$?

[note: Jolly calls this

sodium pentacyanonitrosylferrate(III)]