1. History of Metals in Negative Oxidation States

1891: Discovery that Na metal dissolved Pb, Sb, and Bi in NH₃[1]

1905: Sir James Dewar mixed Fe(CO)₅ with KOH in EtOH to produce crystals in solution that were "at the surface of the liquid at once oxidized by air" forming a brown precipitate. Potentially synthesized K₂[Fe(CO)₄][H₂O].

1907: First suggestion of anionic lead dimers based on conductivity analysis of lead dissolved in an ammonia solution of sodium metal. Suggested existence of "Na⁺⁺" and "Pb₂⁻" in solution.
   Kraus, C. A. J. Am. Chem. Soc. 1907, 29, 1557

1931: Hieber and Leutert report:

\[
\text{Fe(CO)₅} + \text{H₂N} \rightarrow \text{Fe₂(CO)₄(en)₃}{\text{H}^+} \rightarrow \text{H₂Fe(CO)₄}{\text{very pure!}}
\]


1933: Feigl and Krumholz suggest that Hieber's synthesis resulted in an anionic metal carbonyl complex of the form [Fe(en)₃]²⁺[Fe(CO)₄]²⁻.

1938: Hieber and Fack demonstrate that [Ni(o-phen)₃][HFe(CO)₄] and [Ni(o-phen)₃][Co(CO)₄] were strong electrolytes in methanol and acetone.
   Hieber, W., et. al. Z. Anorg. Allg. Chem. 1938, 236, 83

1940's: Hieber synthesizes pyrophoric Na[Co(CO)₄] and Na₂[Fe(CO)₄] from the corresponding hydrides and sodium amide in liquid ammonia.

1947: First unambiguous report of a stable free metal anion: \(^6\text{Li}^+\) and \(^7\text{Li}^+\) identified in gas phase via negative ion mass spec after bombardment of a Ni surface with positive Li ions.
   Sloane, R. H., et. al. Nature 1947, 159, 302

1957: Hieber establishes the correct formula for his 1931 synthesis as [Fe(en)₃]²⁺[Fe(CO)₄]²⁻. Therefore establishing this complex as the first isolated compound to contain a metal in a negative oxidation state.
   Hieber, W., et. al. Chem. Ber. 1957, 90, 286
2. Ligand Considerations
- Most negative oxidation state metals exist as ligand-stabilized complexes.
- Transition metals in negative oxidation states exist exclusively as ligand stabilized complexes
- "As a metal center becomes more electron-rich or highly reduced, all acceptor ligands are expected to become less innocent in character, if they survive intact" - Ellis, J. E. *Inorg. Chem.* 2006, 45, 3167

![Diagram of strained olefin](image)

Formal Ni(-II)

Reality: closer to Ni(II) w/ two norbornene dianions

Interestingly, these complex react as if they were a reservoir of Li$^0$
(More on this later!)


![Diagram of Zr complex](image)

Formal: [Zr(bpy)$_3$]$^2^-$

Reality: Closer to Zr(IV) with 3 bpy dianion ligands


3. Metal Carbonyl Anions
- Many deeply reduced transition metals exists as carbonyl complexes
- Excellent π-back bonding enables synthesis and isolation of anionic metal complexes. Characterizable by IR and X-ray crystallography.

\[
\text{M} = \left[ \begin{array}{c} \text{O} \\ \text{C} \\ \text{O} \end{array} \right] \quad \text{M = CO} \quad \text{M} = \left[ \begin{array}{c} \text{O} \\ \text{C} \\ \text{O} \end{array} \right]
\]

**General Synthetic Strategies**

A. Hieber Base Reaction
\[
\text{Fe(CO)$_5$} + \text{NaOH} \rightarrow \text{Na}[\text{HFe(CO)$_4$}] + \text{CO}_2
\]

B. Alkali Metal Reduction
\[
\text{Fe(CO)$_5$} + 2\text{Na}^0 \rightarrow \text{Na}_2[\text{Fe(CO)$_4$}] + \text{CO}
\]
Heiber, V. W., et. al. *Naturforsch.* 1959, 146, 132

C. Reductive Carbynlation
\[
\text{Mg}^0/\text{Zn}^0, \text{I}_2 + \text{VCl}_3 \rightarrow [\text{Mg(py)$_n$}]^{+2} + 2 [\text{V(CO)}_6]^-
\]

D. Ligand Exchange from Alkali Metal Sandwich Complexes
\[
\text{MX}_n + \text{AC}_{10}H_{8} (n +1 \text{ equiv}) \rightarrow \text{A}^{+}(\text{DME})_x + \text{CO (1 atm) } \rightarrow \text{A}^{+}[\text{M(CO)}_m]^{-}
\]
\begin{align*}
\text{DME} & \quad -60 \degree C \\
\text{A} &= \text{Na}, \text{K}
\end{align*}

Ellis, J. E., et. al. *Organometallics* 1983, 2, 388

- Ligands that are great π acceptors can host much of the negative charge of the complex leading to a *formal* negative oxidation state for many complexes
- **Key Lesson**: Oxidation numbers/states are merely formalisms!
Sampling of Known Metal Carbonyl Anions in Various Oxidation States
(See Ellis, J. E. *Organometallics* 2003, 22, 3322 for a more comprehensive list and excellent discussion as well as reactivity)

(-1): [Co(CO)₄]⁻, [Rh(CO)₄]⁻, [Mn(CO)₅]⁻, [V(CO)₅]⁻, [Ta(CO)₆]⁻
(-2): [Fe(CO)₄]²⁻, [Os(CO)₄]²⁻, [Cr(CO)₅]²⁻, [W(CO)₅]²⁻, [Ti(CO)₆]⁻²
(-3): [Co(CO)₃]³⁻, [Re(CO)₄]³⁻, [Nb(CO)₅]³⁻, [V(CO)₅]³⁻, [Ta(CO)₆]⁻³
(-4): [Cr(CO)₄]⁴⁻, [Mo(CO)₄]⁴⁻, [W(CO)₅]⁴⁻

- Many are extremely air sensitive and pyrophoric solids and exist as Na, K, or Cs salts. However, some are more stable.
- Those in lower oxidations states (Ta, Nb in -3) are at times "treacherous solids that exploded with little or no provocation."
- Reactivity mimicks that of a grignard/strong base


Operational Requirements:
- Argon/Nitrogen atm purified by BASF catalyst, anhydrous MgCl₂, and molecular sieves.
- Ammonia and HMPA twice distilled over CaH then Na⁰
- Drybox for handling the air sensitive solutions

Synthesis via Direct Alkali Metal Reduction

\[
\text{[Re}_2\text{(CO)}_{10}] \xrightarrow{\text{Na}^0 \text{ (6 equiv)}} \text{HMPA, r.t., 12 h} \xrightarrow{\text{NH}_3, \text{-78 °C}} \text{Na}_3\text{[Re(CO)}_{4}] \quad 98\%
\]

NH₃, -78 °C

0.1 Torr

760 Torr Ar

Alternative HMPA-Free Synthesis

\[
\text{[Re}_2\text{(CO)}_{10}] \xrightarrow{\text{Na}^0 \text{ (10 equiv)}} \text{THF, r.t., 1 h} \quad \text{Na}_3\text{[Re(CO)}_{4}] \quad 98\%
\]

- Harder to crystallize in THF
- Generally less pure

Reactivity of Na₃[Re(CO)₄]

\[
\begin{align*}
\text{[H(CH₃)Re(CO)₄]} & \xrightarrow{Tso} \text{OTs} \quad \text{TsO} \quad \text{Re}^- \quad \text{[PPh₄]} \\
\text{Na₃[Re(CO)₄]} & \quad \text{[H(CH₃)Re(CO)₄]} & \quad \text{[PPh₄]} \quad \text{TsO} \\
\text{[H(CH₃)Re(CO)₄]} & \xrightarrow{\text{HMPA, 5 °C}} (\text{2 equiv}) \quad \text{PH₄PCl (1 equiv)} \quad \text{THF} \\
\text{1) EtOH (1 equiv)} & \quad \text{2) MeOTs (1 equiv)} \quad \text{3) PH₄PCl (3 equiv)} \\
\text{2) PH₄PCl (2 equiv)} & \quad \text{2) PH₄PCl (2 equiv)} \quad \text{H₂[Re(CO)₄]} \\
\text{[PPh₄]} & \quad \text{Na₃[Re(CO)₄]} \quad \text{[PPh₄]} \quad \text{H₂[Re(CO)₄]} \\
\end{align*}
\]

Unstable and largely characterized by IR

Famous Metal Carbonyl Anions:

Collman's Reagent: Na₂[Fe(CO)₄]

- First synthesized by Hieber in 1959 by alkali metal reduction (Na Hg amalgam) of Fe(CO)₅ affording the pyrophoric solid, Na₂[Fe(CO)₄] (vida supra).
- In 1973, Manning P. Cooke, a post doc in the lab of James P. Collman (Stanford) accidentally discovered that this reagent can convert alkyl halides into aldehydes. *(Collman, J. P. Acc. Chem. Res. 1973, 8, 342)*

Me⁻¹ \[\text{Na}_2\text{[Fe(CO)}_{4}] \xrightarrow{\text{Me}^-} \text{Me^-}\text{expected} \quad \text{Me^-}\text{observed}

- In 1973, Collman patented a simpler route to Na₂[Fe(CO)₄] as a means to drive new research on this reagents synthetic applications

Fe(CO)₅ + Na⁰ \[\text{Ph}_2\text{C=O} \xrightarrow{\text{Dioxane, 100 °C}} \text{Na}_2\text{Fe(CO)}_{4}]

4. Applications of Carbonyl Anions in Synthetic Methodology

**4a: Collman’s Reagent Selected Applications**
Conversion of Alkyl Bromides to Aldehydes

\[
\begin{align*}
\text{Na/Hg Amalgam} & \quad \text{Fe(CO)}_5 (1.4 \text{ equiv}) \\
& \quad \text{PPh}_3 (1.2 \text{ equiv}) \\
\text{THF, 0 - r.t., 3 h - 48h} \\
R = \text{alkyl} \\
\end{align*}
\]

\[
\text{in situ generation of} \quad \text{Na}_2[\text{Fe(CO)}_4] \quad \text{then substrate addn}
\]

50 - 99%

**Synthesis of Aliphatic Ketones**

\[
\begin{align*}
\text{Na}_2[\text{Fe(CO)}_4] (1 \text{ equiv}) \\
\text{NMP} \\
\text{(Slight excess)} \\
R = \text{alkyl} \\
X = \text{Br, OTs, C(O)Cl}
\end{align*}
\]

\[
\text{Collman, J. P., et. al.} \\
\text{J. Am. Chem. Soc. 1972, 94, 1788}
\]

31 - 80%

**Synthesis of Carboxylic Acids, Esters and Amides**

\[
\begin{align*}
\text{R} = n-C_{12}H_{25} \\
\text{84%} \\
\text{O}_2 \\
\text{then H}^+ \\
\text{EtOH} \\
\text{R} = n-C_{8}H_{17} \\
\text{89%}
\end{align*}
\]

\[
\text{McMurry, J. E., et. al.} \\
\text{Tetrahedron 1981, 37, 319}
\]

1,2-Diketones from Alkylbromides

1) \( \text{Na}_2[\text{Fe(CO)}_4] (1 \text{ equiv}) \)
   
   CO (1 atm)
   
   THF, r.t.

2) \( \text{CuCl} (2 \text{ equiv}) \)
   
   \( \text{N}_2 \text{ atm, THF, r.t.} \)

For detailed mechanism:

**Carbonylative Reductive Heck-Type Cyclizations**

\[
\begin{align*}
\text{Br} \\
\text{Me} \\
\text{Na}_2[\text{Fe(CO)}_4] (1 \text{ equiv}) \\
\text{then H}^+ \\
\end{align*}
\]

**Application in Total Synthesis!**

First use of \( \text{Na}_2[\text{Fe(CO)}_4] \) in synthesis!

\[
\text{Aphidicolin} \\
\text{McMurry, J. E., et. al.} \\
\text{Tetrahedron 1981, 37, 319}
\]

Desired

Undesired

55% 1 : 1 mixture
Double Alkylation of Fullerene


- Impressively, the second electrophile adds since the nucleophilicity of iron is significantly weakened when it has a transient C₆₀ ligand...
- No reaction with unactivated alkyl halides.

**K₂[Fe(CO)₄]** as a Safer Alternative to **Na₂[Fe(CO)₄]**

$$\text{Fe(CO)₅} \xrightarrow{\text{KOH (2 equiv)}} \text{K[Fe(CO)₄]} + \text{KHCO₃} \xrightarrow{\text{THF, reflux}} \text{K₂[Fe(CO)₄]} + \text{CO, H₂} + \text{Fe(CO)₅(PB₃)₂}$$

- Nonpyrophoric
- Not soluble in THF, but soluble in DMA
- Moisture sensitive but degradation product can be washed away
- Same reactivity as Collman's Reagent


**4b: Other Metal Carbonyl Anions in Synthetic Methodology**

Hieber anion: **[Fe(CO)₅]NO⁺**

"Viewed" as iron(II) with cationic NO Ligand but not entirely true*

**Synthesis:**

$$\text{Fe(CO)₅} \xrightarrow{\text{ANO}_2 (1 \text{ equiv})} \text{MeOH} \xrightarrow{\text{A = Alkali Metal}} \text{A[Fe(CO)₅(NO)]}$$

A = Alkali Metal


**Reality of Ground State Electronics:** Plietker, B., et. al. *ACIE 2014*, **53**, 1790

Reactions of Neutral Pi-Allyl Complexes with Carbon Nucleophiles and Electrophiles

$$\text{TBA[Fe(CO)₃(NO)]}$$

1) Mel, 1,3-butadiene THF (or DMF), r.t.


2) **P(OR)₃**

3) THF, 60 °C

DMF, 75 °C

Further reading and other substrate classes:


Amination of Neutral Pi-Allyl Complexes

$$\text{MeBr} \xrightarrow{\text{TBA[Fe(CO)₃(NO)]}} \text{DCM, 0 °C}$$


$$\text{R}^* = (-)-menthyl$$

- Other enantiomer gave opposite stereochemical outcome as expected

$$\text{82%} \quad >98\% \text{ de}$$
Application in Total Synthesis!

\[
\begin{align*}
\text{Ph} & \quad \text{OTBS} \\
\text{Me} & \quad \text{Me} \\
\text{MesO} & \quad \text{Me}
\end{align*}
\]

\[
\begin{align*}
\text{HN} & \quad \text{HN} \\
\text{Ph} & \quad \text{Me} \\
\text{Me} & \quad \text{Me}
\end{align*}
\]

**Ionomycin Total Synthesis:** Kocienski, P. J., et. al. Angew. Chem. 2009, 121, 5122

**Side Chain Synthesis:** Kocienski, P. J., et. al. Org. Biomol. Chem. 2006, 4, 3325

**Rationale for Reagent Choice:**
- Cationic pi-allyls from Fe and Mo gave poor yields.
- Pi-allyls from anionic iron gave neutral diastereomeric complexes that were separable by column chromatography

**4c: Halophilic Attack of Metal Carbonyl Anions**


**Suggestive of aryl carbanion intermediates**


Yields relative to 100% total yield of [Fe] containing compounds

- Other metal carbonyl anions portrayed similar behavior (Mn, Re)

**Catalytic Allylic Displacement**

TBA[Fe(CO)₃(NO)] (2.5 mol %)

\[
\begin{align*}
\text{t-BuO} & \quad \text{R} \\
\text{O} & \quad \text{R}
\end{align*}
\]


**Mechanism**

PDT

CO₂

ROH

Nu-H

Fe"\text{L}_{n}

\[
\begin{align*}
\begin{array}{c}
\text{NHC's & divergent regiochemistry} \\
\text{A} & \quad \text{B}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\text{A: } & \quad \text{B: } \\
\text{93} & \quad \text{7}
\end{align*}
\]


PhCH(Et)CN

Ph

23%
5. Other Sources of Metal Anions

**BY NO MEANS EXHAUSTIVE**

5a: Anionic Metal Olefin/Arene Complexes via Alkali Metal Reduction

**Dilithium Nickel Olefin Complexes**

\[
\text{Ni}^0 + 2 \text{Li}^0 \rightarrow (\text{THF})_2 \text{Li}^+ \rightarrow \text{Li}(\text{THF})_2^-
\]

Formal \(\text{Ni}^{II}\)


**Dilithium Iron Ethylene Complex**

\[
\text{Fe}^{II} + 4 \text{Li}^0 \rightarrow \text{(TMEDA)}\text{Li}^+ \rightarrow \text{Li}(\text{TMEDA})^{-}
\]

Formal \(\text{Fe}^{II}\)


**Metal Anthracene Complexes as First Row TM Metal Anion Synthons**

\[
\text{Co}^{II} \text{Br}_2 + \text{KCl} \rightarrow \text{Co}^{II}\text{Cl} + \text{KBr}
\]

Formal \(\text{Co}^{II}\)


---

**Application Toward Synthesis of [COD$_2$Co]$^+$**

\[
\text{COD} (1 \text{ equiv}) \quad \text{K}^+ (18\text{-crown-6})
\]

Excess COD

\[
\text{Et}_2\text{O}, 20^\circ\text{C}
\]

91%

**Alternatively...**

\[
\text{KC}_{14}\text{H}_{10} (3 \text{ equiv}) \quad \text{Co}^{II} \text{Br}
\]

18-crown-6 (1 equiv)

-78°C - 20°C

77% but impure

Complex originally reported as lithium salt by Jonas, K., et. al. *Angew. Chem. Int. Ed.* 1976, 15, 767

---

**5b: Direct Target Ligand Reduction then Metal Capture**

\[
\text{Me}_2\text{P} = \text{P} = \text{Me}_2 \quad \text{Li}^0 (\text{Excess}) \rightarrow \text{Ru}^{II}\text{COD(acac)$_2$}
\]

THF, 25°C

- X-ray crystal data more suggestive of a higher valent complexes with two radical anion ligands.

---

[Co(cot)$_2$]$^+$ [Co(dppe)$_2$]$^+$ [Co(CN$_3$)$_2$]$^+$ [Co(P(OMe)$_3$)$_4$]$^+$ [Co(CO)$_4$]$^+$

- 75% 75% 83% 92% 87%

- Easier access to homoleptic anionic metal complexes via facile ligand exchange

- Also used to access other homoleptic/heteroleptic anionic metal complexes


---


Formal Ru(-II)

But really Ru$^0$
6. Reactivity and Applications of Other Metal Anions in Synthetic Methodology

6a: Inate Reducing Ability of Dilithium Metal-Pi Complexes

\[
\text{Biphenyl (2 equiv)} \rightarrow [\text{Li(THF)}_2)_2\text{Ni(COD)}_2]_{\text{THF}}^\text{H}_2 \\
\text{Ni(COD)}_2 + 2 \text{Li[Biphenyl]} \rightarrow I_2 \rightarrow [\text{Li(THF)}_2)_2\text{H}_2\text{Ni(COD)}_{1,5}]_{\text{THF}} \\
\text{Ni(COD)}_2 + 2 \text{LiI}
\]

- Great reducing ability through its ability to act as Li\(^0\) source.


6b: Alkene Hydrogenation

\[
\text{R} = X, R' \rightarrow [\text{K}^+(\text{DME})_2]_{\text{THF}} (1-5 \text{ mol%}) \\
\text{R} = X, R' \rightarrow \text{H} \rightarrow \text{H} \rightarrow \text{most at r.t.}
\]

60% at 80°C

- After activation with ligand, main electronic state of cobalt is Co(I). Neutral Cod acts as a place holder for other ligands.
- Suspect catalyst activation by partial hydrogenation of COD to afford a cobalt hydride species with 2nd order rate dependence.


diip = diisopropylphenyl

Problems with Protic Substrates:

Cobaltate Quench After 1st Turnover

\[
\text{L}_n\text{Co}^\text{I} \rightarrow \text{K}^+(\text{DME})_2 \rightarrow L_n\text{Co}^\text{I} \\
\text{X = N,O} \\
\text{R} \rightarrow \text{XH} + 1/2 \text{H}_2 \\
\text{X} \rightarrow \text{XK} + 1/2 \text{H}_2
\]


Less active hydrogenation catalyst requiring harsher conditions

Catalyst Oxidation via SET

\[
\text{Ph} \rightarrow \text{Me} \rightarrow \text{OH} \rightarrow \text{OH} \\
(33 \text{ mol%}) \\
\text{THF, r.t., 3h}
\]

Yield relative to theoretical 2 e\(^-\) transferred from catalyst

6b: Amine-Borane Transfer Hydrogenation

\[
\text{Me} \rightarrow \text{ nitrogen} \rightarrow \text{NMe} \rightarrow \text{NMe} \\
\text{Ar-N} \rightarrow \text{N-Ar} \rightarrow \text{N-Ar} \\
\text{Co cat (5 mol %)} \\
\text{NH}_3\text{BH}_2 (1 \text{ equiv}) \\
\text{THF, 25°C, 16h} \\
\text{Co cat} \\
- \text{Ar = Mes, diipp}
\]

6. Cross Coupling with Well Defined Metal Complexes in Negative Oxidation States

\[
\begin{align*}
R' & \quad \text{Br} \\
(1 \text{ equiv}) & \\
\text{BrMg}^{-} & \quad \text{R''} \\
(2.4 \text{ equiv}) & \\
\text{THF}, -20^\circ C, 5 \text{ mins} & \quad \text{R', R''} \\
[\text{Li(TMEDA)}]_2\text{Fe(C}_2\text{H}_4\text{)}_4 & \quad (5 \text{ mol \%}) & \quad 67 \text{ - } 96\% \\
\end{align*}
\]


\[\text{X = Br, Cl, I} \]
(1 equiv)

\[\text{BrMg}^{-} \quad \text{R} \quad \text{(5 mol\%)} \]

\[\text{THF/NMP, r.t., 16 h} \quad \text{R} \quad \text{(7 - 47\%)} \]


\[\text{X = Br, Cl, F, OTf} \]
(1 equiv)

\[\text{BrMg}^{-} \quad \text{R} \quad \text{(1.5 equiv)} \]

\[\text{MTBE, -65 \degree C} \quad \text{R} \quad \text{(41 - 85\%)} \]


7. Some Exotic Applications

Dinitrogen activation

\[\text{R}_2\text{P}^{-}\text{FePR}_{2} \quad \text{KC}_8 \quad \text{(1 equiv)} \quad \text{THF, then 18-crown-6} \quad \text{R}_2\text{P}^{-}\text{FePR}_{2} \quad \text{ClMe}_2\text{Si} \quad \text{SiMe}_2\text{Cl} \quad \text{75\%} \]


8. Outlook on the Field

- Metals in negative oxidation states have been known for several decades and many synthetic routes are known.
- Field is largely confined to the physical and inorganic realms.
- Few albeit exciting applications of these species as reagents for chemical synthesis.
- Sensitivity of the reagents are a potential barrier to more widespread research.
- Identification of ligands that can support a formal negative oxidation state while also conferring reagent stability could be key factors for making useful catalysts out of these species.