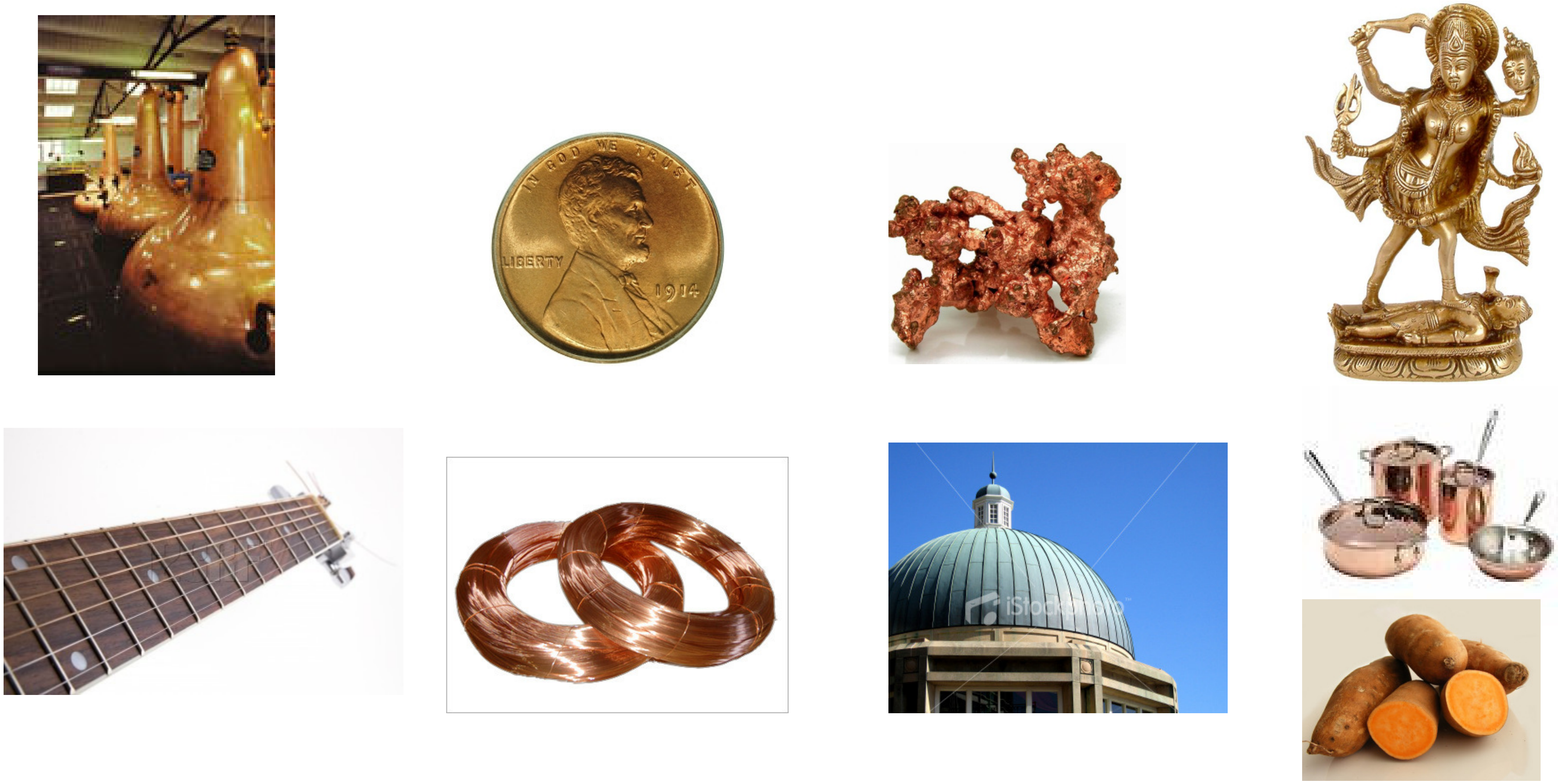
Copper Chemistry

Cu : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$



F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochman, *Advanced Inorganic Chemistry*, 6th ed., John Wiley, New York, pp. 855-864.

- Cu has a single *s* electron in its *fourth* shell. One may be inclined to think, based on its electronic configuration, that it has similar properties to the alkali metals, in particular K, however this is not the case.

- The filled *d* shell is much less effective than a filled *p* shell at shielding the *s* electron from the nuclear charge (*29 protons*), such that the first ionization energy of Cu is higher than that of its closest alkali relative K (*19* protons).

$$\mathbf{K} : 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 4s^1$$

$$\Big\downarrow\ 4.34\ \text{eV}$$

$$\mathbf{K}^+ : 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6$$

$$\Big\downarrow\ 31.63\ \text{eV}$$

$$\mathbf{K}^{\mathbf{2+}} : 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^5$$

$$\mathbf{Cu} : 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 4s^1\, 3d^{10}$$

$$\Big\downarrow\ 7.73\ \text{eV}$$

$$\mathbf{Cu}^+ : 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^{10}$$

$$\Big\downarrow\ 20.29\ \text{eV}$$

$$\mathbf{Cu}^{\mathbf{2+}} : 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^9$$

Ionization energies (eV)

- In contrast, the second (and third) ionization energy of Cu is much lower than that of K. **Why ?**

- Its valence *d* electrons give Cu transition metal character with the existence of highly colored paramagnetic Cu(II) complexes having a d^9 valence band configuration.
- The *d* shell electrons impart *noble* character to Cu complexes resulting in *covalent character* justifying its Group 11 position in the periodic table relative to the highly *ionic* group 1 alkali metals. As a result solid state Cu systems display higher lattice energies than the alkali metals, consistent with its smaller atomic radius:

Na^+	0.95 Å
K^+	1.33 Å
Cu^+	0.93 Å

- The high covalency of elemental Cu, as a result of its interatomic *sigma*-bonding, contributes to its *high thermal and electrical conductivity* (only second to Ag).

Cu(II)

- Cu(II) is the ***more stable*** state of copper
- Configuration $3d^9$ with one unpaired electron ***(paramagnetic)***
- Incomplete 3*d* subshell permits *d-d* state-to-state electronic transitions, which causes color ***(typically blue or green)***

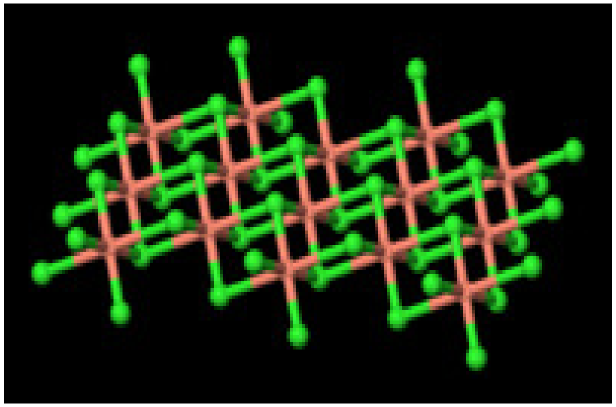
vs.

Cu(I)

- Cu(I) is an ***unstable*** state of copper
- Configuration $3d^{10}$ with no unpaired electrons ***(diamagnetic)***
- Complete 3*d* subshell precludes *d-d* state-to-state transitions, so Cu(I) is ***colorless*** like isoelectonic Zn(II), unless they are paired with a paramagnetic anion.

Cu(II)

- Most copper(II) compounds exhibit distortions from idealized octahedral geometry due to the *Jahn-Teller effect*.
- In $CuCl_2(H_2O)_2$ the copper can be described as a highly distorted O_h complex, the Cu(II) center being surrounded by two water ligands and four chloride ligands, which bridge asymmetrically to other Cu centers.
- Copper(II) chloride dissociates in aqueous solution to give the blue color of $[Cu(H_2O)_6]^{2+}$ and yellow or red color of the halide complexes of the formula $[CuCl_{2+x}]^{x-}$. Concentrated solutions of $CuCl_2$ appear green because of the combination of these various chromophores (re. Cu(II) carbonates and *verdigris*)



Cu(I)

- Although CuCl is insoluble in water, it dissolves in aqueous solutions containing suitable Lewis base donors.
- It forms complexes with halide ions, for example forming H_3O^+ $CuCl_2^-$ with concentrated hydrochloric acid. It also dissolves in solutions containing CN^-, $S_2O_3^{2-}$, and NH_3 to give corresponding complexes.
- Although only poorly soluble in water, its aqueous solutions are unstable with respect to disproportionation into Cu and $CuCl_2$. In part for this reason samples in air assume a green coloration.

Oxidation of Cu(I)

- In aqueous solution, *Cu(I) is readily oxidized to Cu(II) in the presence of oxygen* *(re*: cytochrome c oxidase)

$$
\begin{array}{ll}
4(\mathrm{Cu}^{+} \rightarrow \mathrm{Cu}^{2+} + e^{-}) & E^{o}_{\mathrm{Ox}} = -\,0.153\ \mathrm{V} \\
\mathrm{O}_2 + 4\mathrm{H}^{+} + 4\,e^{-} \rightarrow 2\mathrm{H}_2\mathrm{O} & E^{o}_{\mathrm{Red}} = +\,1.229\ \mathrm{V} \\
\hline
4\mathrm{Cu}^{+} + \mathrm{O}_2 + 4\mathrm{H}^{+} \rightarrow 4\mathrm{Cu}^{2+} + 2\mathrm{H}_2\mathrm{O} & E^{o}_{\mathrm{cell}} = \ \ 1.076\ \mathrm{V}
\end{array}
$$

- Moreover, *Cu(I) undergoes spontaneous disproportionation*:

$$
\begin{array}{ll}
\mathrm{Cu}^{+} \rightarrow \mathrm{Cu}^{2+} + e^{-} & E^{o}_{\mathrm{Ox}} = -\,0.153\ \mathrm{V} \\
\mathrm{Cu}^{+} + e^{-} \rightarrow \mathrm{Cu} & E^{o}_{\mathrm{Red}} = +0.521\ \mathrm{V} \\
\hline
2\,\mathrm{Cu}^{+} \rightarrow \mathrm{Cu} + \mathrm{Cu}^{2+} & E^{o}_{\mathrm{cell}} = +\,0.368\ \mathrm{V}
\end{array}
$$

- Thus $\Delta G°$ (= $-nFE°$) is negative, i.e. spontaneous for disproportionation.

Stabilizing Cu(I) in Compounds

- Simple Cu(I) compounds that can exist in the presence of water are those with *low-charge anions whose compounds are insoluble in water*:

CuCl, CuBr, CuI, and CuCN,

- In the solid, *stability depends on* the neighboring anion and the resulting *lattice energy* of the ionic solid.

- Copper(I) chloride is made by boiling a solution of HCl(*aq*) and $CuCl_2(aq)$ in the presence of excess Cu.

- *Synthesis takes advantage of the stability of solid CuCl*, which makes redox between Cu and Cu^{2+} spontaneous:

$$Cu(s) + Cu^{2+}(aq) + 2Cl^{-}(aq) \rightarrow 2\,CuCl(s) \qquad E^{o}_{cell} = +0.442\text{ V}$$

- In concentrated HCl solution, the actual product is ?

?

- In concentrated HCl solution, the dichlorocuprate ion, $[CuCl_2]^-$, is the actual product:

$$Cu(s) + Cu^{2+}(aq) + 4\ Cl^-(aq) \rightleftharpoons 2\ [CuCl_2]^-(aq)$$

- On dilution with water, copper(I) chloride precipitates:

$$[CuCl_2]^-(aq) \rightleftharpoons CuCl(s) + Cl^-(aq)$$

- Conversely, if $CuCl(s)$ is added to a chloride solution, it will dissolve due to the driving force of forming the $[CuCl_2]^-(aq)$ complex.

- The equilibrium can be displaced in either direction.
- In the synthesis, *formation of* $[CuCl_2]^-(aq)$ *drives the equilibrium to the right* (LeChatelier’s Principle).
- Anions or bridging ligands that form complexes with Cu^+ may stabilize Cu^+ so long as they do not form more stable complexes with Cu^{2+}.
- When CuCl(*s*) is treated with ethylenediamine (en) Cu^+ is oxidized to Cu^{2+} because *……………..?*

Copper(I) Iodide

- *Copper(I) iodide precipitates when any Cu(II) salt is added to a KI(aq) solution*.

$$2\mathrm{Cu}^{2+}(aq) + 4\mathrm{I}^{-}(aq) \rightarrow 2\mathrm{CuI}(s) + \mathrm{I}_2$$

- I^{-}(*aq*) is a strong enough reducing agent to reduce Cu^{2+} (*aq*) to CuI (*s*):

$$\begin{array}{ll}
2\mathrm{I}^{-} \rightarrow \mathrm{I}_2 + 2e^{-} & E^{o}_{\mathrm{Ox}} = -\,0.54\ \mathrm{V} \\
2(\mathrm{Cu}^{2+} + \mathrm{I}^{-} + e^{-} \rightarrow \mathrm{CuI}) & E^{o}_{\mathrm{Red}} = +\,0.88\ \mathrm{V} \\
\hline
2\mathrm{Cu}^{2+} + 4\mathrm{I}^{-} \rightarrow 2\mathrm{CuI} + \mathrm{I}_2 & E^{o}_{\mathrm{cell}} = +\,0.34\ \mathrm{V}
\end{array}$$

An element of surprise—efficient Cu-functionalized dye-sensitized solar cells

- Dye-sensitized solar cells with carboxylate-derivatized {Cu^IL_2} complexes are surprisingly efficient and offer a long-term alternative approach to ruthenium-functionalized systems.

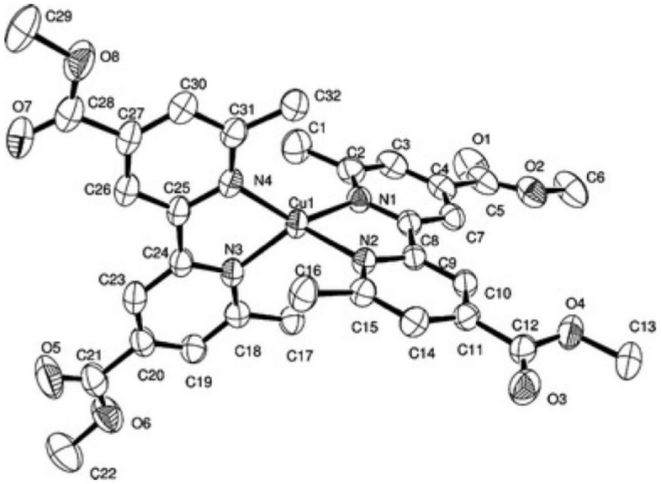
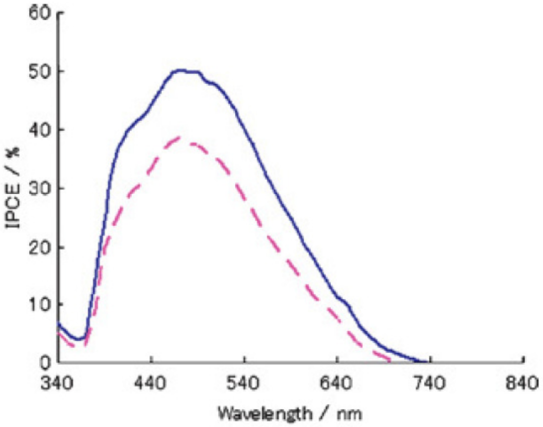
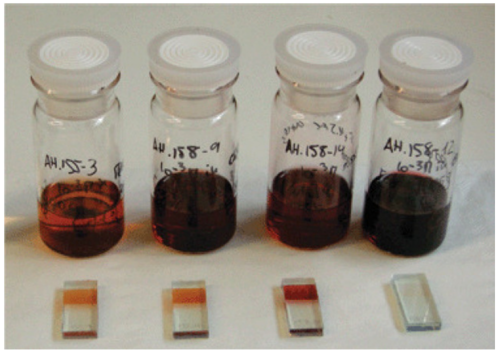


Fig. 1 Solid state structure of the $[Cu(\mathbf{3})_2]^+$ cation present in $[Cu(\mathbf{3})_2][PF_6]$ showing the numbering scheme adopted; hydrogen atoms have been omitted for clarity, thermal ellipsoids depicted at 50% probability. Selected bond lengths (Å) and angles (°): Cu1–N1, 2.009(2); Cu1–N2, 2.016(2); Cu1–N3, 2.039(3); Cu1–N4, 2.003(3); N1–Cu1–N2, 80.93(10); N1–Cu1–N3, 122.14(10); N2–Cu1–N3,





Cu(I)-Catalyzed Carboxylative Coupling of Terminal Alkynes, Allylic Chlorides, and CO_2

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Scheme 2. N-Heterocyclic Carbene Copper(I) Complexes

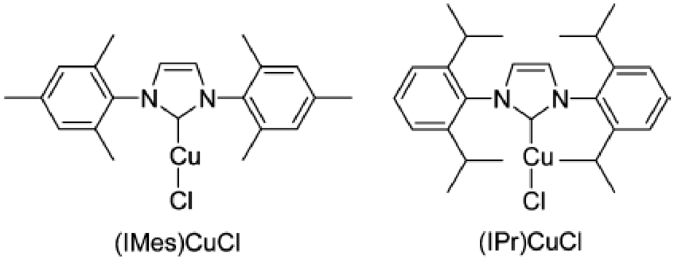
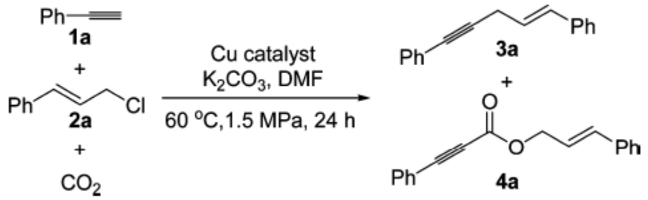


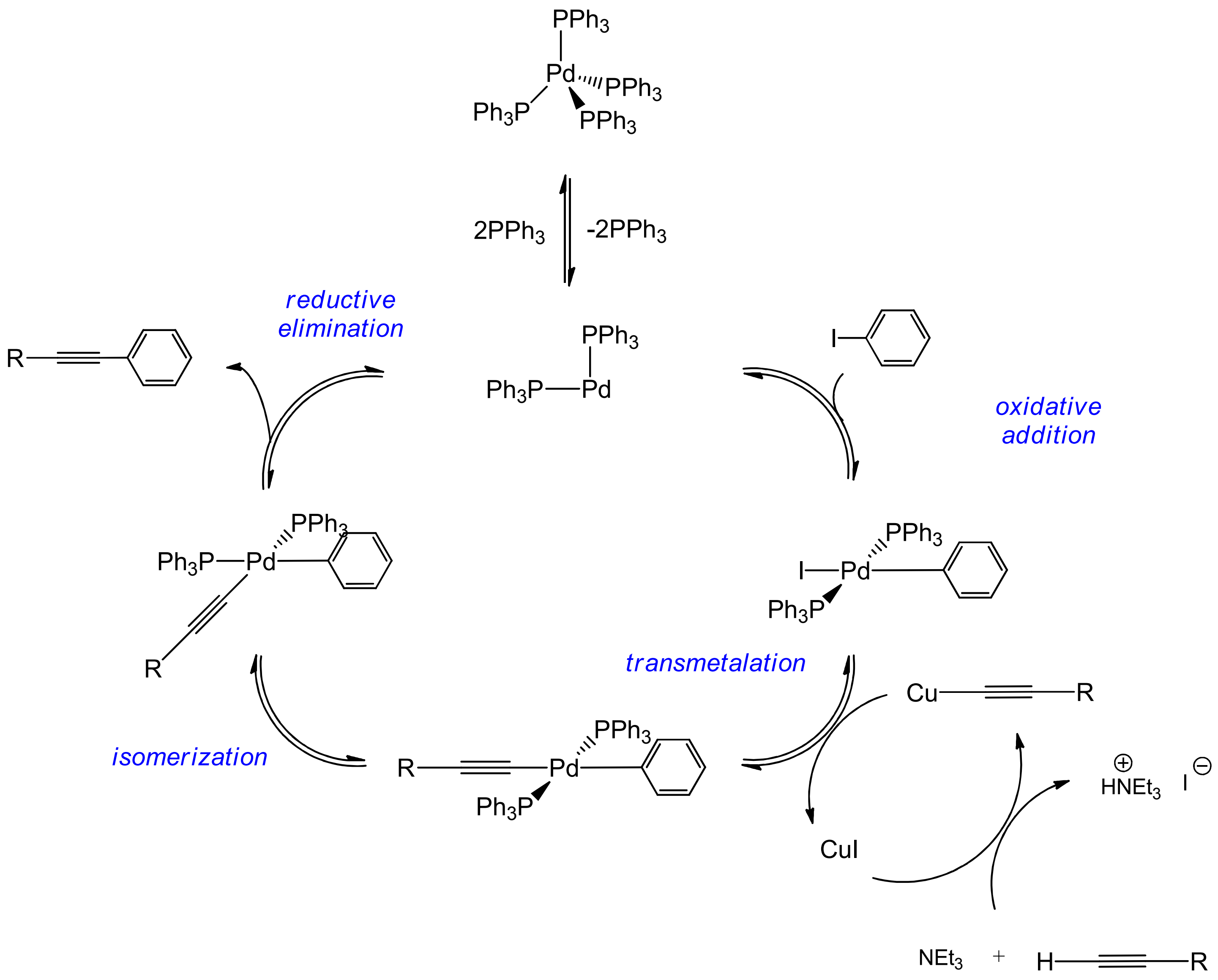
Table 1. Copper-Catalyzed Carboxylative Coupling of Phenylacetylene, Cinnamyl Chloride, and CO_2[a]



entry	catalyst	yield (%)[b] 3a	yield (%)[b] 4a
1[c]	-	-	-
2	CuCl	10	46
3	CuBr	35	47
4	CuI	28	24
5	CuCl + bpy	23	52
6	CuCl + TMEDA	12	68
7	(IMes)CuCl	3	51
8[d]	(IPr)CuCl	<1	91
9[e]	(IPr)CuCl	<1	74
10[f]	(IPr)CuCl	17	-
11[g]	(IPr)CuCl	8	26

[a] Reaction conditions: **1a** (2 mmol), **2a** (3 mmol), K_2CO_3 (4 mmol), Cu catalyst (10 mol %), 20 mL of DMF. [b] Isolated yield. [c] In the absence of catalyst. [d] 92% catalyst was recovered after reaction. [e] 5 mol % catalyst. [f] In the absence of CO_2. [g] 0.2 MPa CO_2.

CuI as a co-catalyst in Sonogashira C-C coupling



Cytochrome c oxidase (CcO)
-Nature's fuel cell

$$O_2 \quad + \quad 8H^+ \quad + \quad 4Fe^{2+}(CcO) \longrightarrow 2H_2O \quad + \quad 4H^+ \quad + \quad 4Fe^{3+}(CcO)$$

- Cytochrome c oxidase is responsible for O_2 consumption in Nature.
- This remarkable enzymatic machine activates dioxygen via *proton coupled electron transfer* producing two equivalents of water.