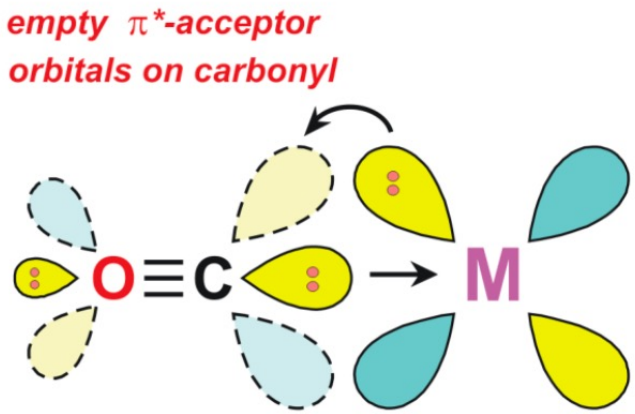
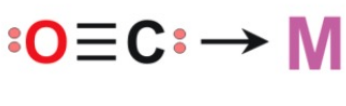
Carbonyl Ligands



powerful π-acceptor ligand!

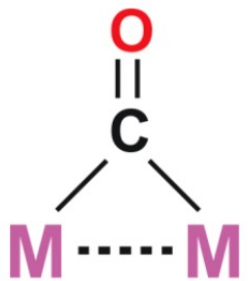
excellent ligand, therefore, for stabilizing electron-rich low-valent metal centers

Standard Bonding Modes:



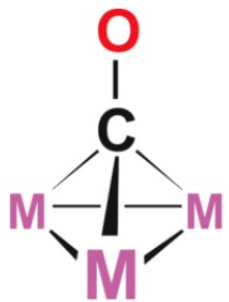
terminal mode

2e⁻ neutral donor



μ_2- *bridging mode*

2e⁻ neutral donor



μ_3- *bridging mode*

3e⁻ neutral donor

Metal carbonyls form one of the oldest (and important) classes of organometallic complexes. Most metal carbonyls are *toxic*!

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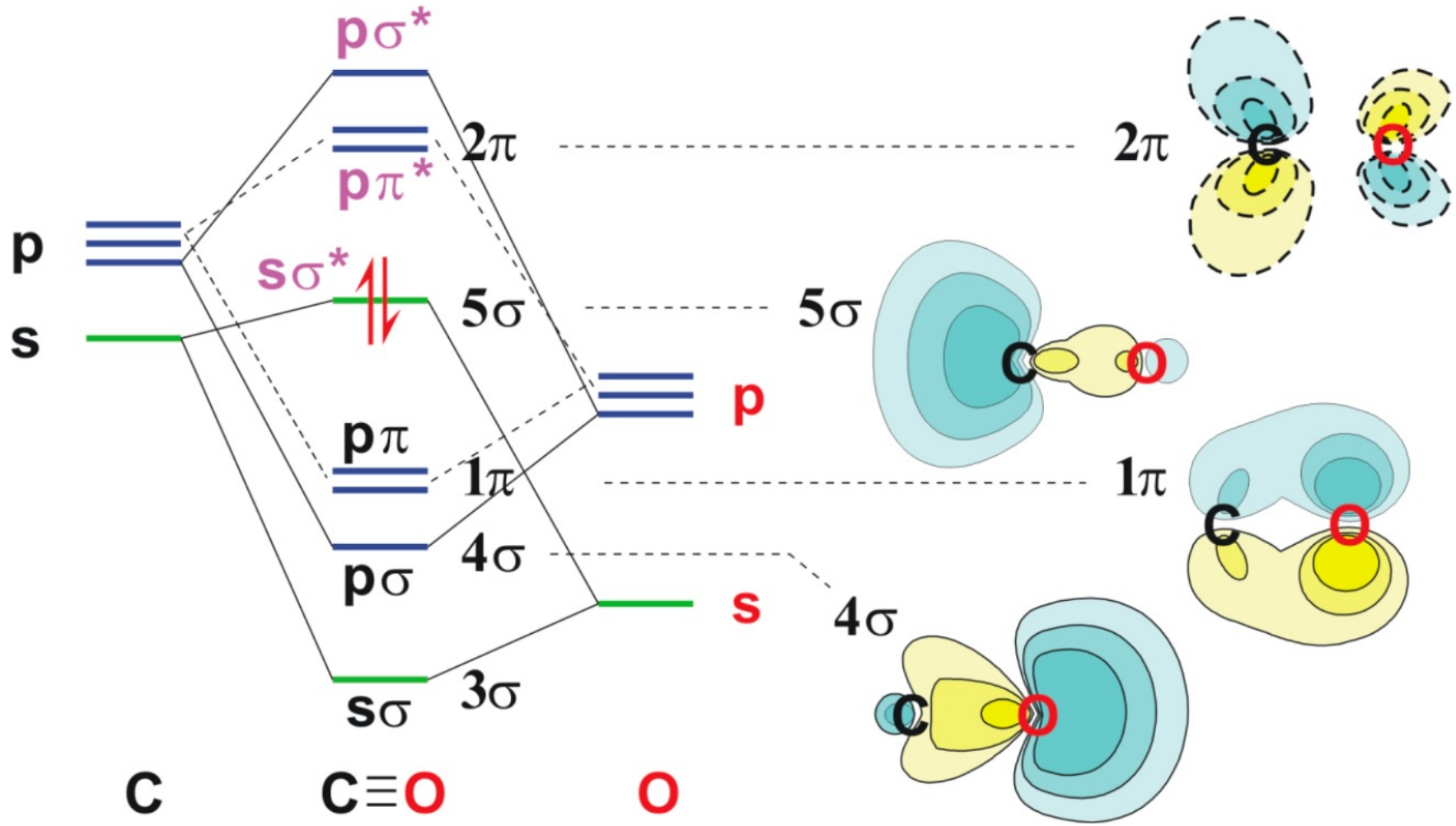
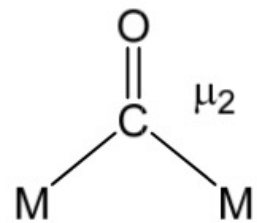
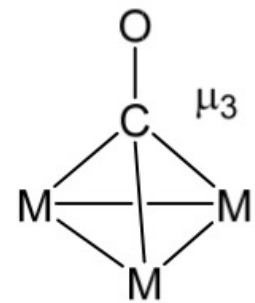
Examples of *neutral*, binary metal carbonyls:

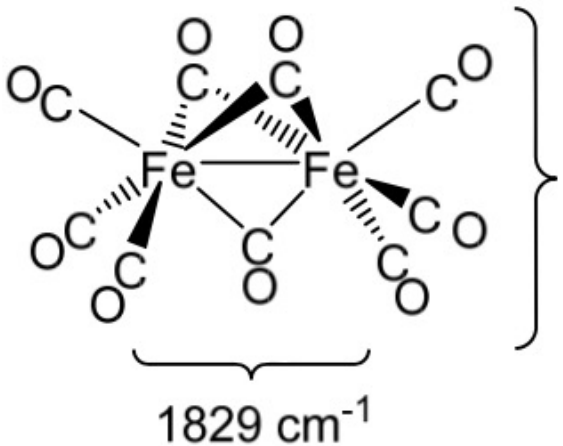
4	5	6	7	8	9	10	11
Ti	$V(CO)_6$	$Cr(CO)_6$	$Mn_2(CO)_{10}$	$Fe(CO)_5$ $Fe_2(CO)_9$ $Fe_3(CO)_{12}$	$Co_2(CO)_8$ $Co_4(CO)_{12}$	$Ni(CO)_4$	Cu
Zr	Nb	$Mo(CO)_6$	$Tc_2(CO)_{10}$	$Ru(CO)_5$ $Ru_3(CO)_{12}$	$Rh_4(CO)_{12}$ $Rh_6(CO)_{16}$	Pd	Ag
Hf	Ta	$W(CO)_6$	$Re_2(CO)_{10}$	$Os(CO)_5$ $Os_3(CO)_{12}$	$Ir_4(CO)_{12}$	Pt	Au

Molecular Orbital Diagram for CO:



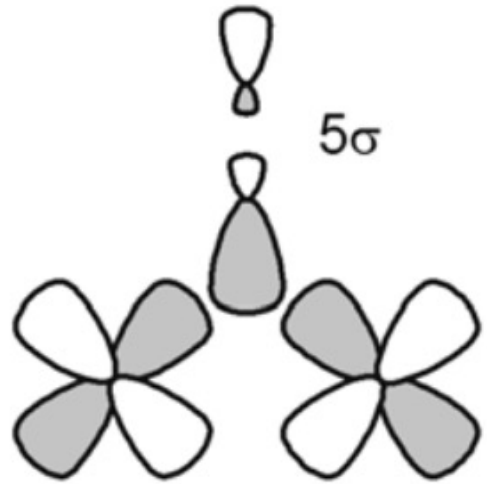
Terminal and bridging CO-groups can be differentiated by IR-spectroscopy:

	free	terminal	bridging	
				
Wave numbers $\tilde{\nu}$ in cm^{-1}	2143	2120 - 1850	1850 - 1750	1730 - 1620

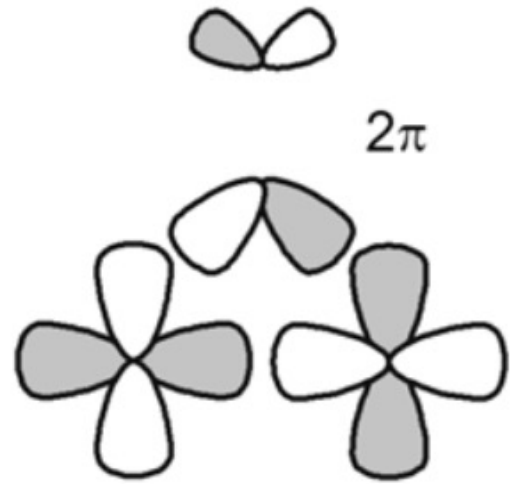


2082, 2019 cm^{-1}

1829 cm^{-1}



σ-Bonding



π-Backbonding

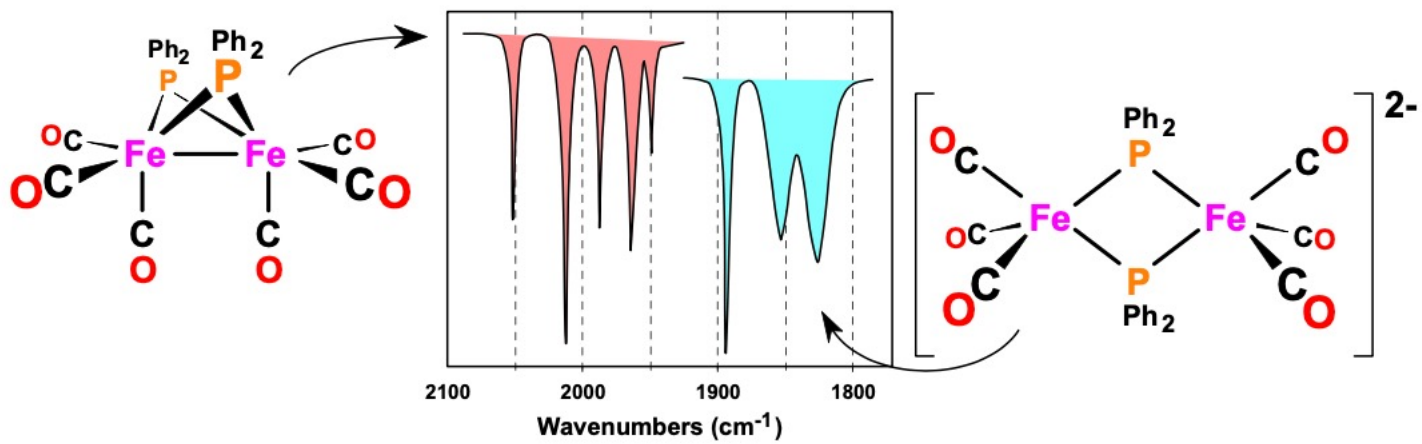
The CO-vibration depends on the strength of the back-bonding from the metal center and correlates with the electron density at the metal and with the energy level of the HOMO‘s respectively.

$\tilde{\nu}$ as a probe:

$Ni(CO)_4$	2060 cm^{-1}	$[Mn(CO)_6]^+$	2090 cm^{-1}
$[Co(CO)_4]^-$	1890 cm^{-1}	$Cr(CO)_6$	2000 cm^{-1}
$[Fe(CO)_4]^{2-}$	1790 cm^{-1}	$[V(CO)_6]^-$	1860 cm^{-1}
		$[Ti(CO)_6]^{2-}$	1750 cm^{-1}

increased π-backbonding

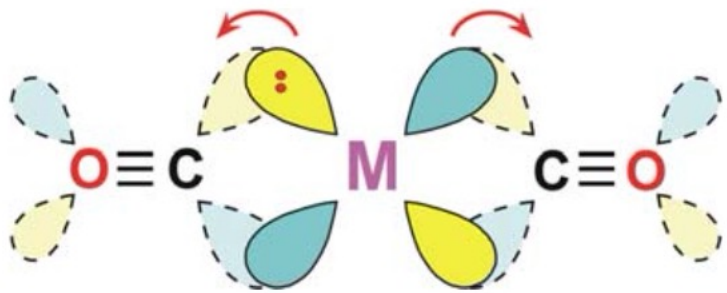
(Attention: only isostructural complexes may be compared)



Donor/Acceptor Characteristics of Other Ligands

L in L-Ni(CO)$_3$	ν (CO)/cm^{-1}
P(*t*-Bu)$_3$	2056
PMe$_3$	2064
PPh$_3$	2069
P(OMe)$_3$	2080
P(OPh)$_3$	2085
PF$_3$	2111

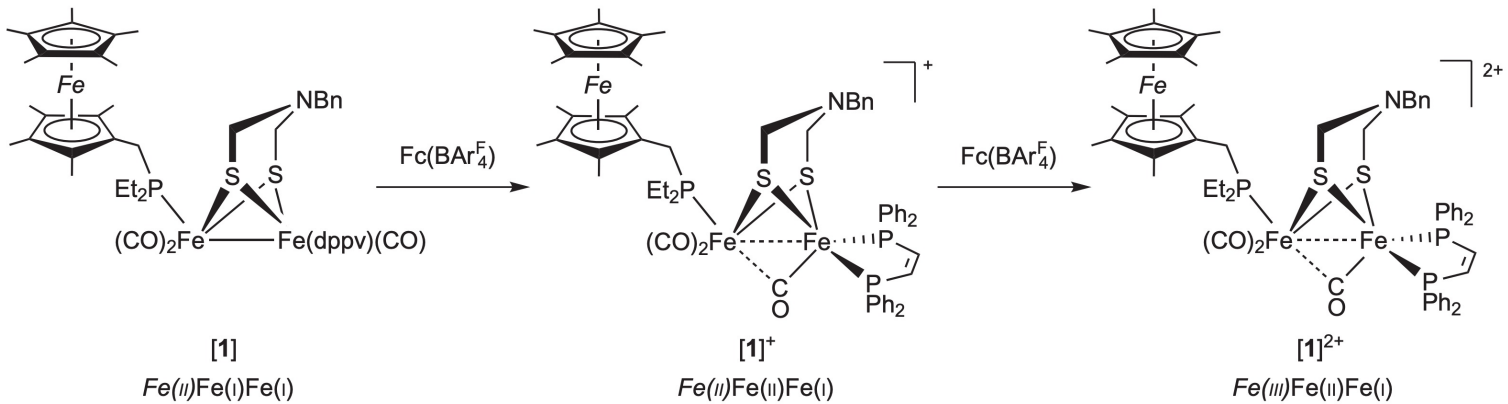
L in L$_3$Mo(CO)$_3$	ν (CO)/cm^{-1}
Pyridine	1746, 1888
CH$_3$CN	1783, 1915
PPh$_3$	1835, 1934
P(OMe)$_3$	1888, 1977
PCl$_3$	1991, 2040
PF$_3$	2055, 2090



See also L-M(CO)$_5$ complexes (M = Cr, Mo, W)

decreasing π-acceptor strength:

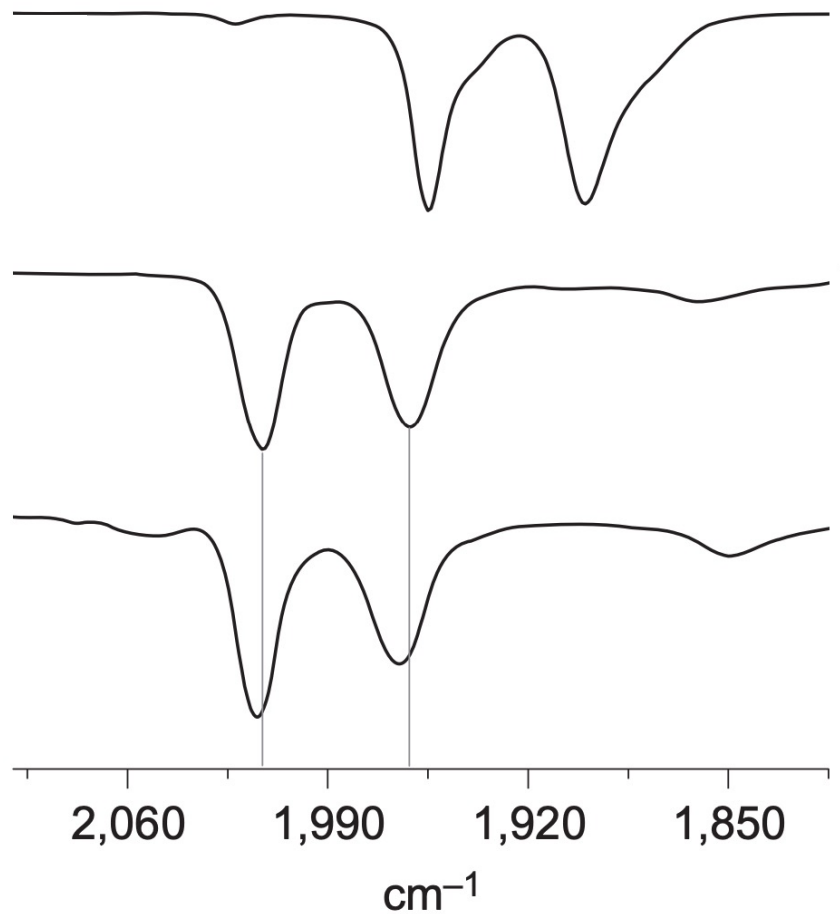
NO > CO > PF$_3$ > RNC > PCl$_3$ > P(OR)$_3$ > PR$_3$ > RCN > NH$_3$

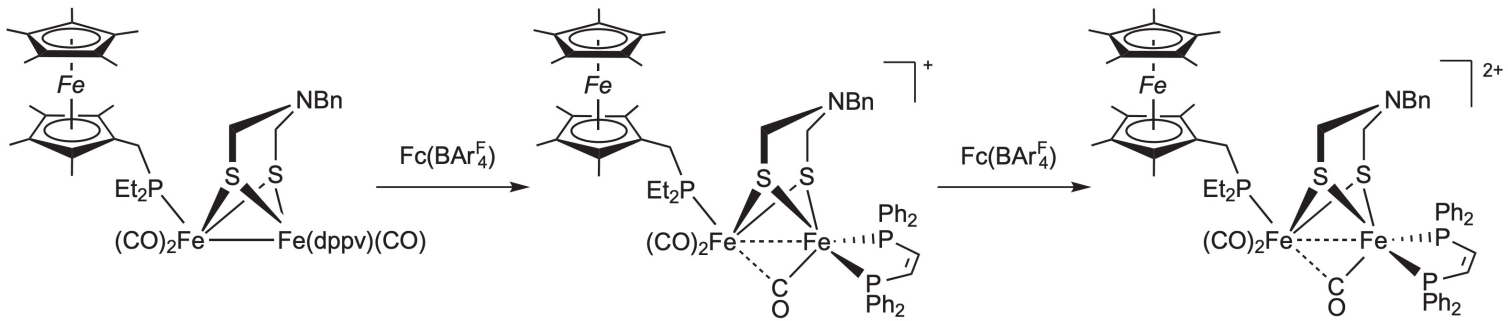


[**1**]
*Fe(II)*Fe(I)Fe(I)

[**1**]$^+$
*Fe(II)*Fe(II)Fe(I)

[**1**]$^{2+}$
*Fe(III)*Fe(II)Fe(I)





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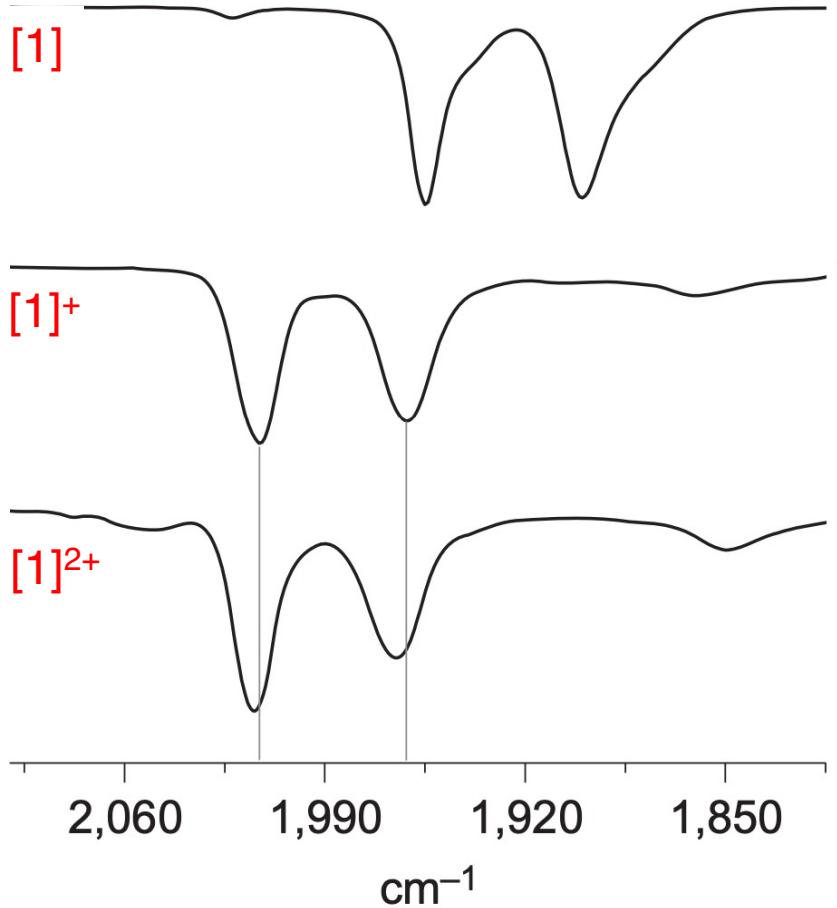
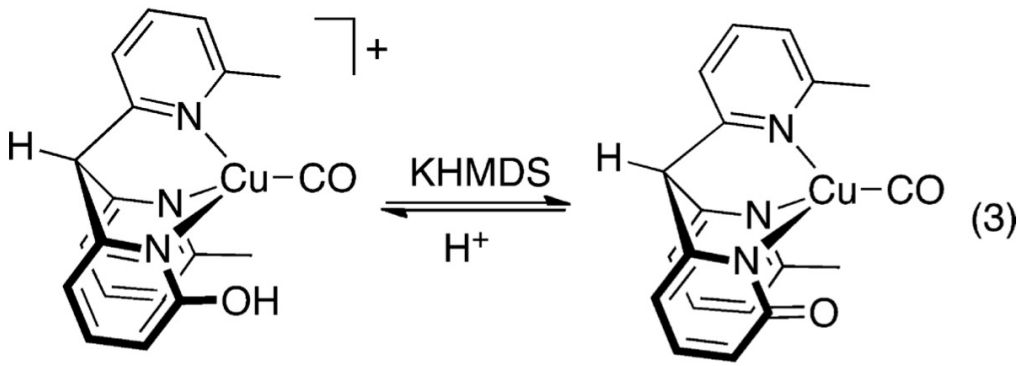
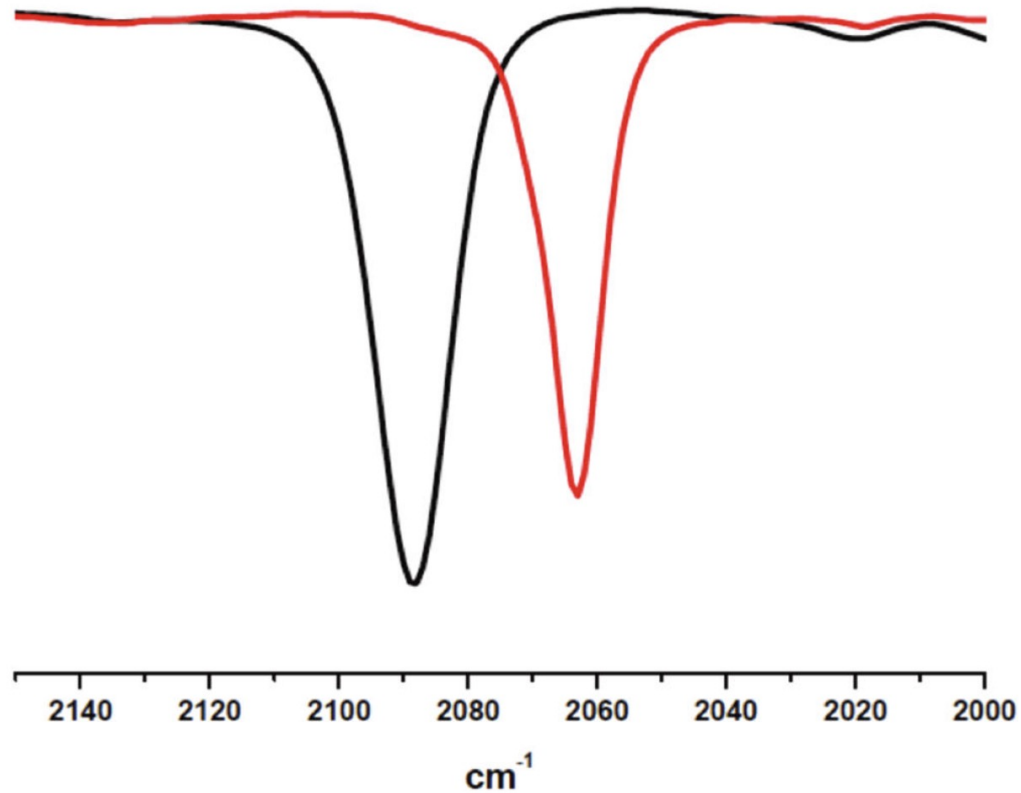
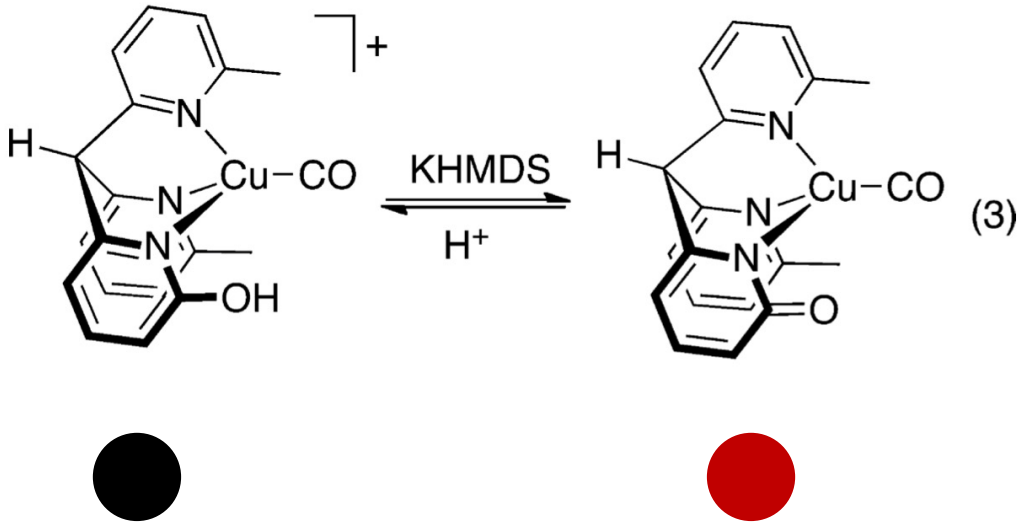


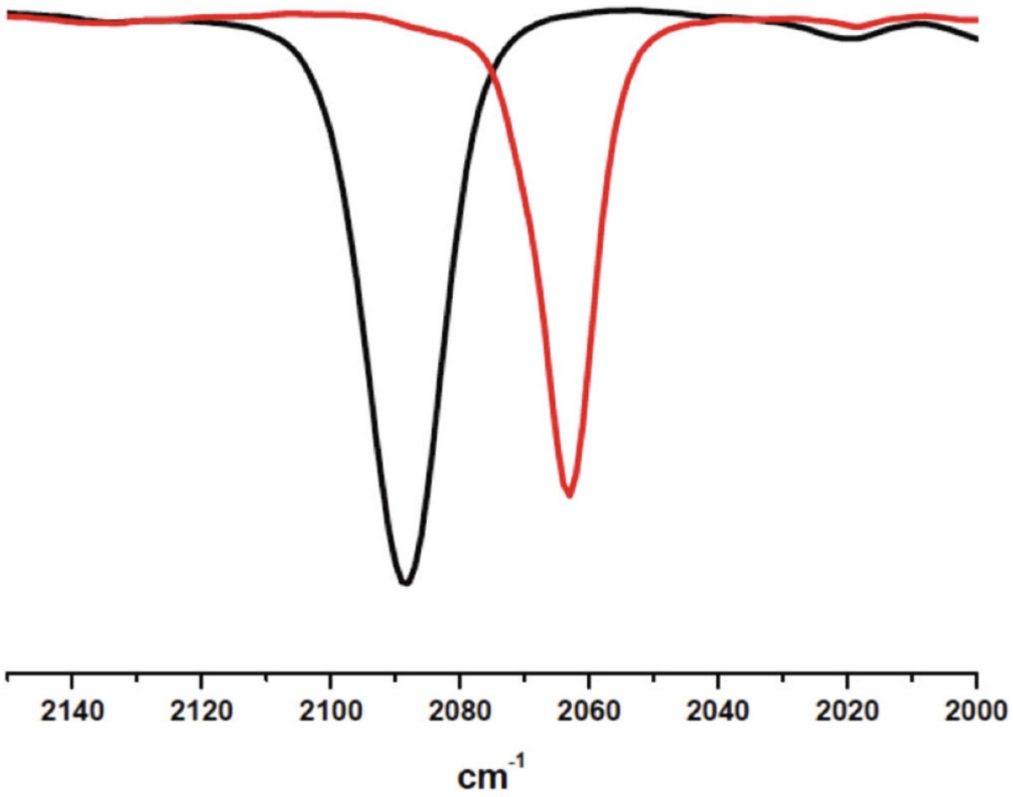

H
N
Cu–CO
N
N
OH
+
KHMDS
H+
H
N
Cu–CO
N
N
O

(3)


2140
2120
2100
2080
2060
2040
2020
2000
cm-1


H
N
Cu–CO
N
N
OH
+
KHMDS
H+
H
N
Cu–CO
N
N
O

(3)


2140
2120
2100
2080
2060
2040
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2000
cm-1