Organometallic Chemistry

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➢ 7 Steps in Mastering Organometallics

- ✓ Periodic Table
- ✓ Ligands
- ✓ Electron Count (18e rule)
- ✓ Oxidative Addition
- ✓ Reductive Elimination
- ✓ β-Hydride Transfer/Elimination
- ✓ Migratory Insertion

Periodic Table

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

Early Middle Late

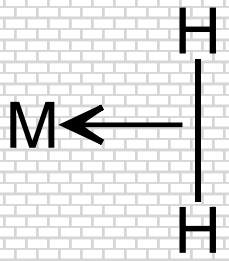
Periodic Table

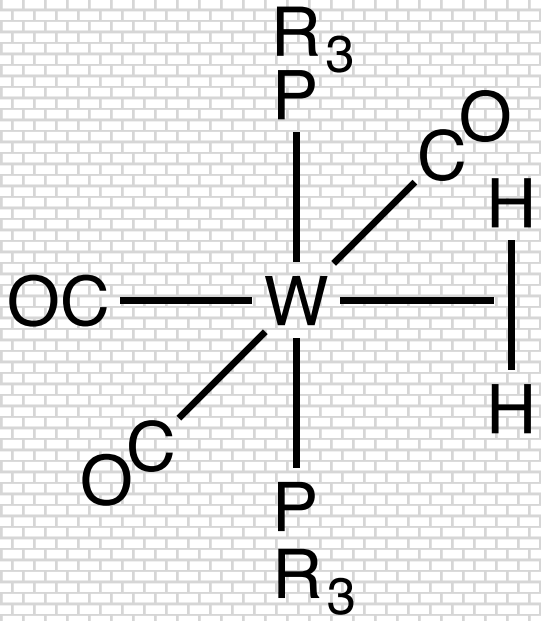
d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
Sc^{2+}	Ti^{2+}	V^{2+}	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
Y^{2+}	Zr^{2+}	Nb^{2+}	Mo^{2+}	Tc^{2+}	Ru^{2+}	Rh^{2+}	Pd^{2+}	Ag^{2+}	Cd^{2+}
La^{2+}	Hf^{2+}	Ta^{2+}	W^{2+}	Re^{2+}	Os^{2+}	Ir^{2+}	Pt^{2+}	Au^{2+}	Hg^{2+}

➢ Ligands

- ✓ Nature of the ligands
- ✓ Charge of the ligands
- ✓ Binding modes
- ✓ Number of electrons donated

Dihydrogen: Neutral 2e donor





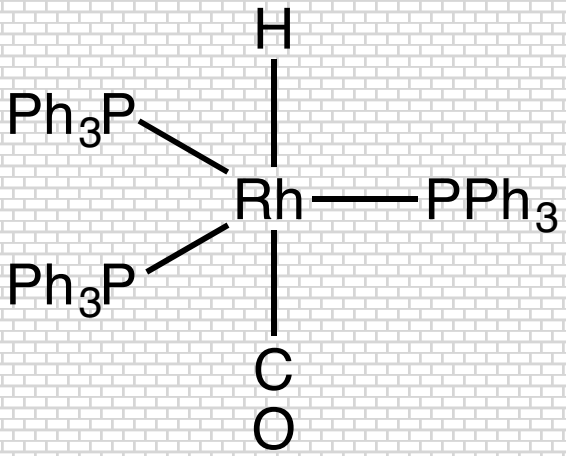
Curious to know?

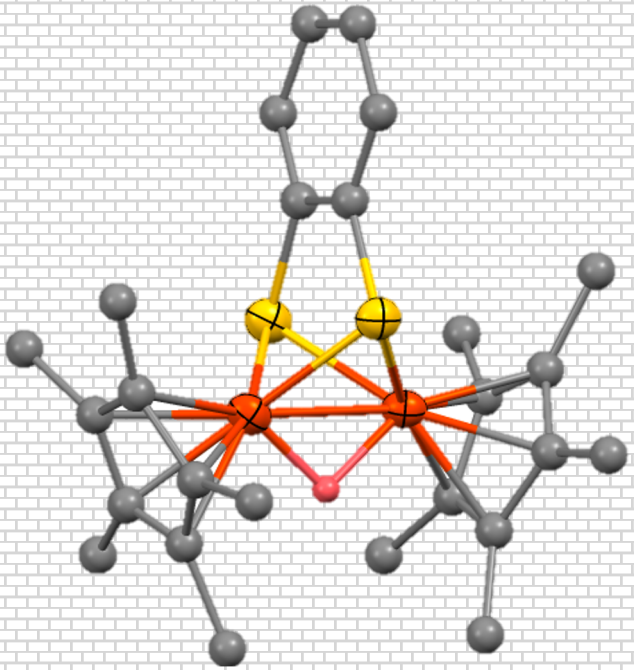
- IR
- NMR
- X-ray Diffraction
- Neutron Diffraction

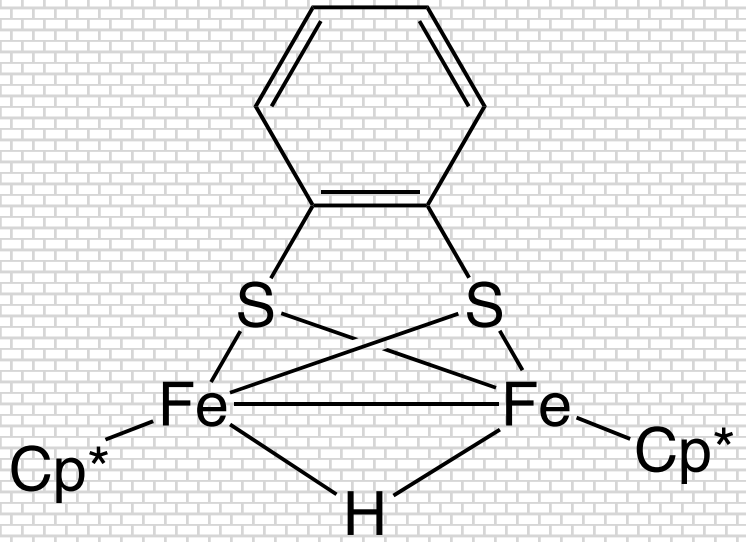
$W(\eta^2\text{-}H_2)(CO)_3[P(i\text{-}Pr)_3]_2$

J. Am. Chem. Soc. 1984, 106, 2, 451–452; *J. Chem. Educ.* 1996, 73, 10, 988

Hydride: Anionic 2e donor





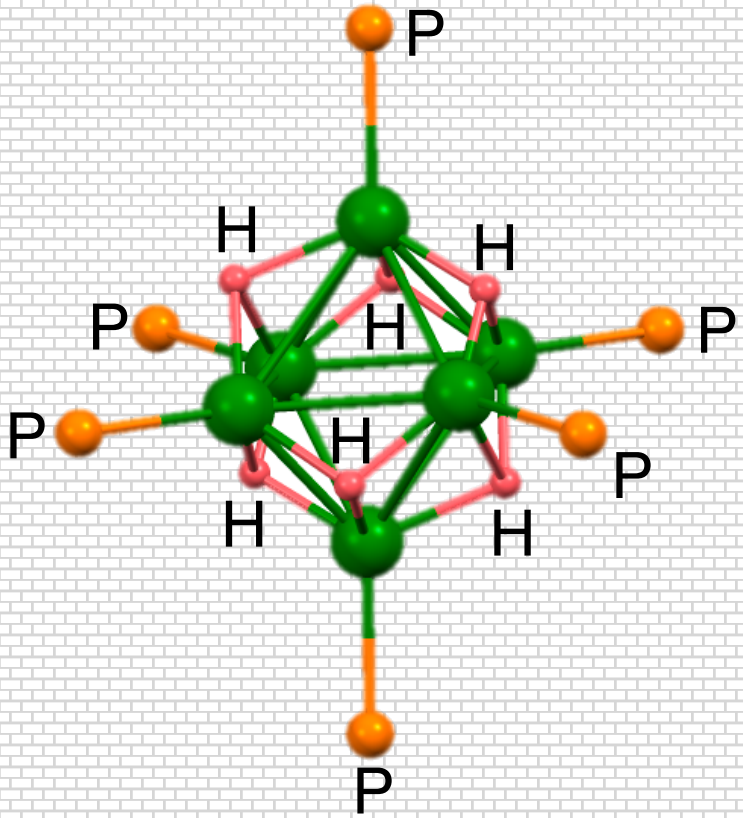


Curious to know?

- What is Cp*

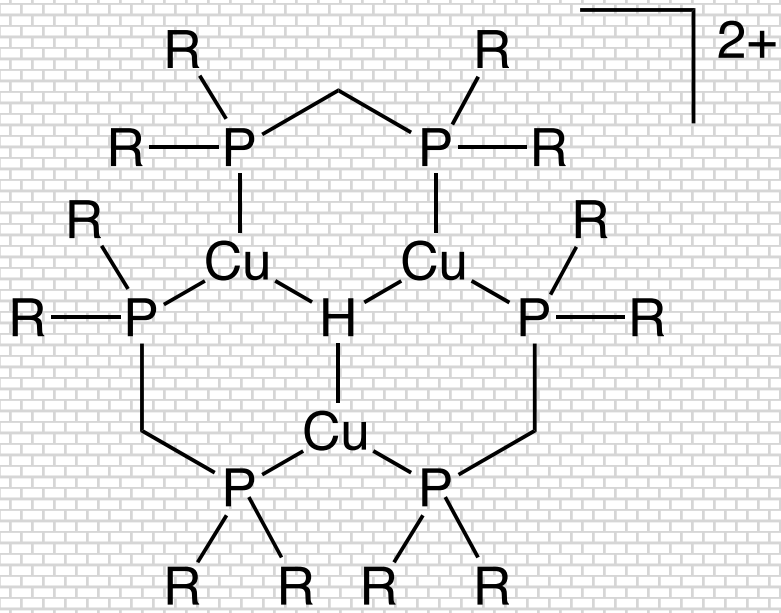
J. Chem. Soc. A, 1968, 3133-3142; *Inorg. Chem.* 2015, 54, 21, 10243–10249

Hydride: Anionic 2e donor



$[(R_3P)Cu(\mu_3\text{-}H)]_6$

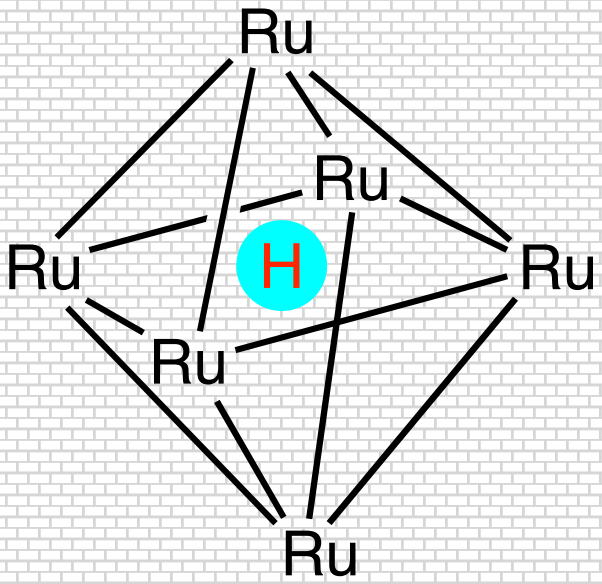
Stryker's reagent



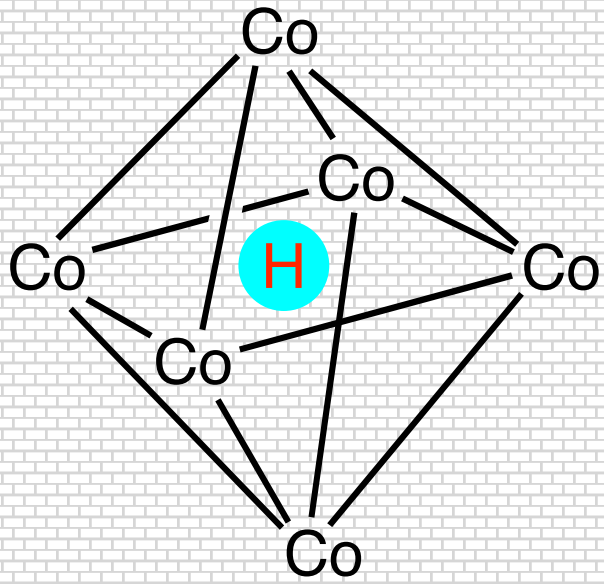
$[Cu_3(dcpm)_3(\mu_3\text{-}H)]^{2+}$

J. Am. Chem. Soc. 1989, 111, 3472–3473; *J. Am. Chem. Soc.* 2005, 127, 4562–4563

Hydride: Anionic 2e donor



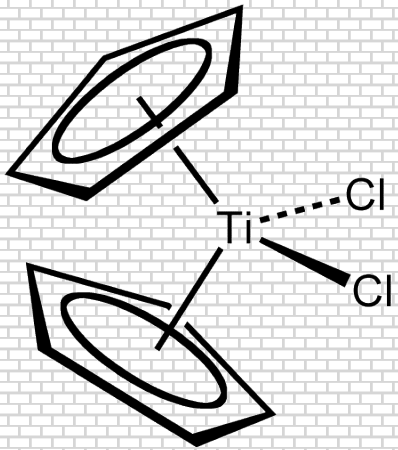
$[HRu_6(CO)_{18}]^-$

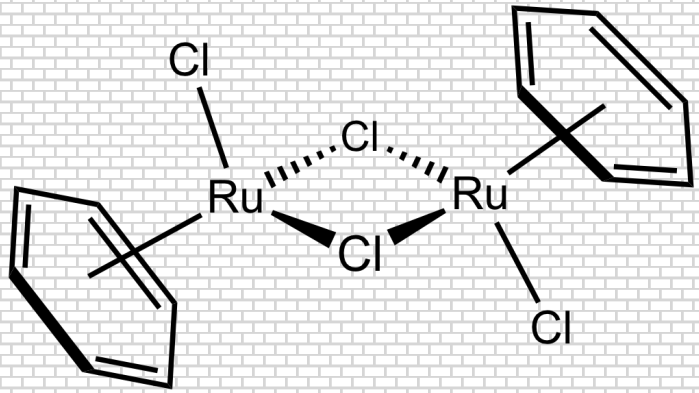


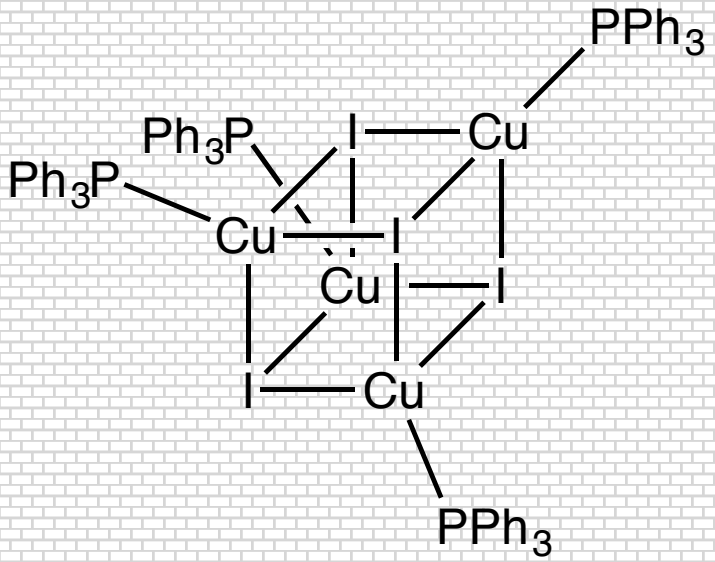
$[HCo_6(CO)_{15}]^-$

J. Chem. Soc., Chem. Commun., 1976, 945-946; Angew. Chem. Int. Ed. 1998, 37, 2193–2197

Halides: anionic 2e, 4e or 6e donor

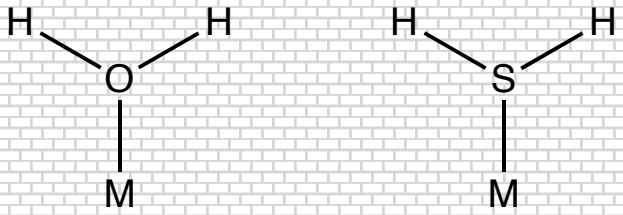


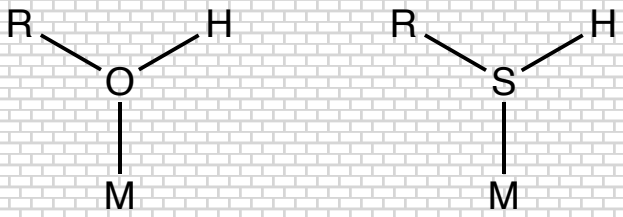


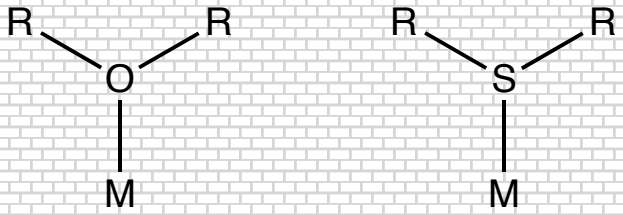


J. Am. Chem. Soc. 76, 4281–4284; *Inorg. Synth.*, 21, 74–78; *Dalton Trans.*, 2019,48, 7899-7909

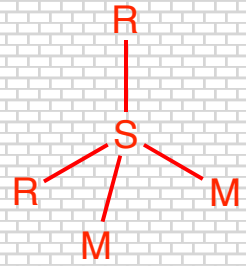
H_2O, ROH, RSH, R_2O, R_2S:

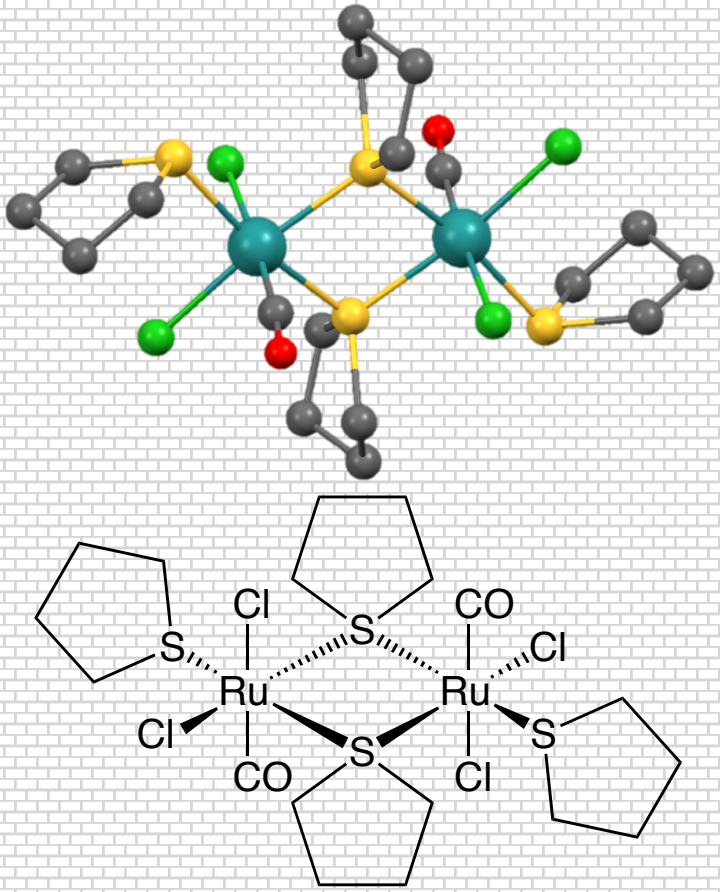






Neutral 2e donors

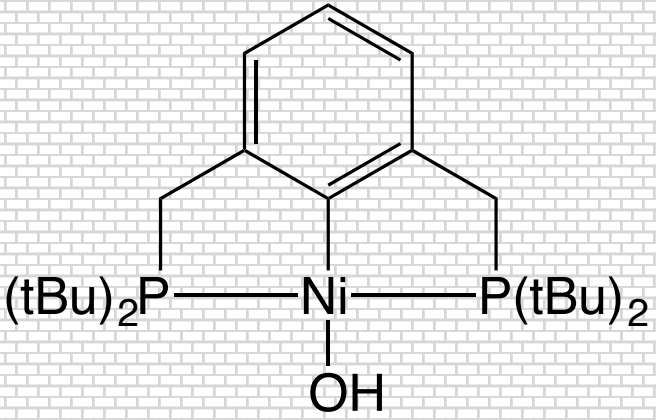




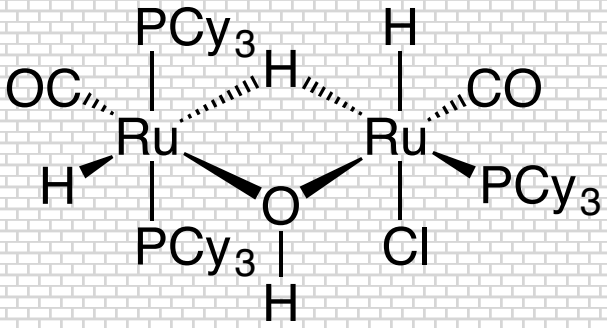
Neutral 2e and 4e donors

Dalton Trans., 2010, 39, 5713–5720

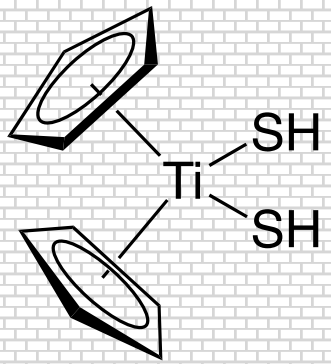
➢ HO^- and HS^-:



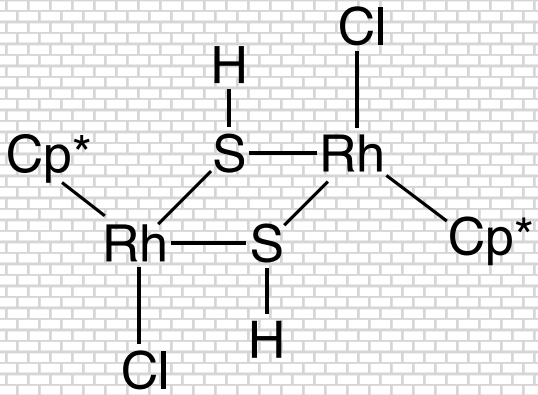
2e donor



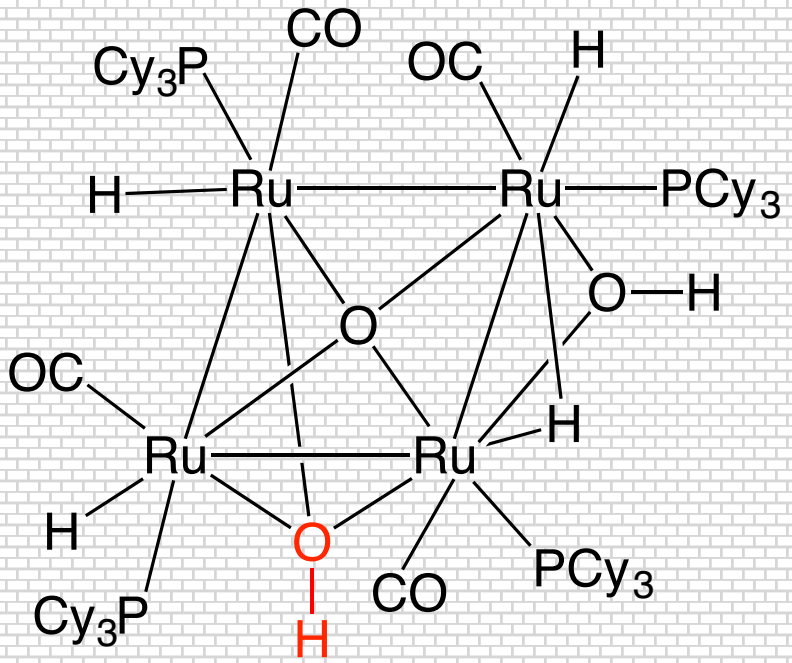
4e donor



2e donor



4e donor

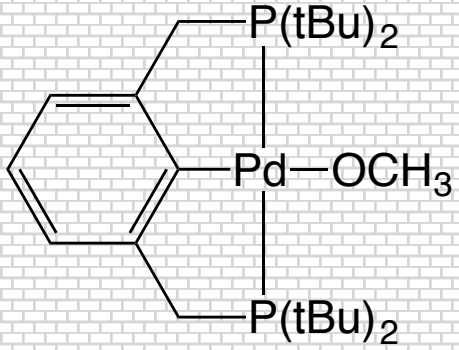


6e donor

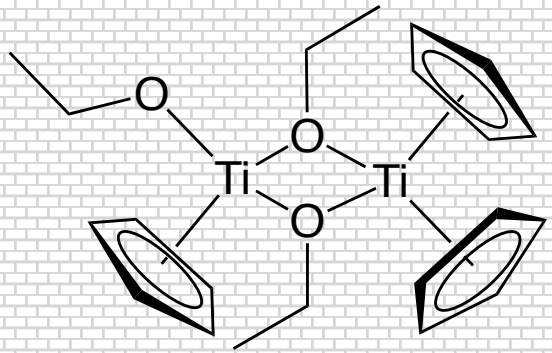
Curious to know about (μ_3-SH) ???

Chem. Eur. J. 2012, 18, 6915 – 6927; *Organometallics* 1985, 4, 524-528;
Organometallics 2006, 25, 1047–1051; *Organometallics* 1997, 16, 151–154

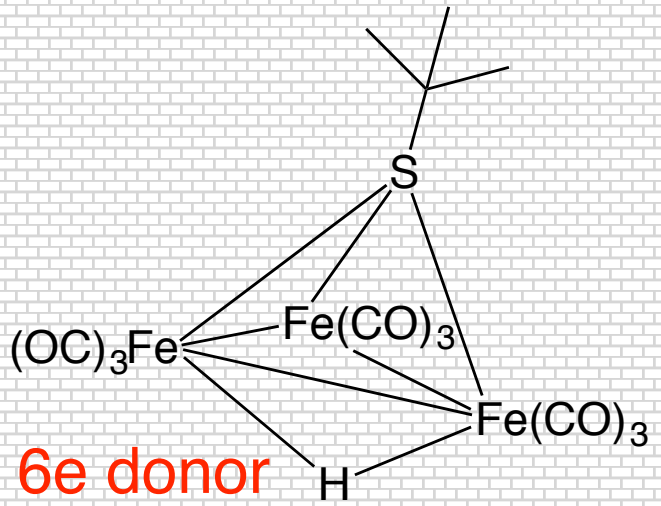
➢ RO^- and RS^-:



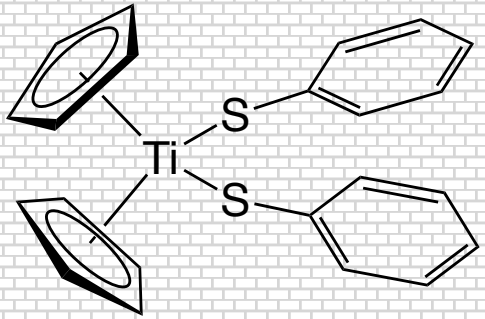
2e donor



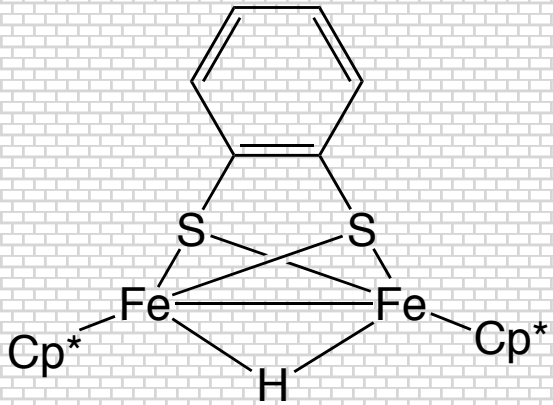
4e donor



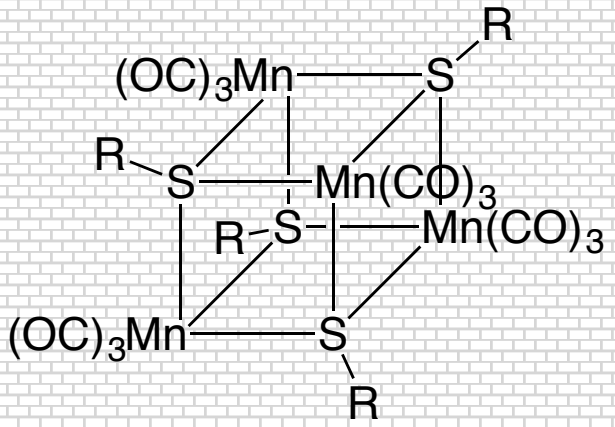
6e donor



2e donor



4e donor



Curious to know about (μ_3-OR) ???

J. Am. Chem. Soc. 2011, 133, 17713–17726; *Inorg. Chem.* 2017, 56, 3324–3334; *Inorg. Chem.* 2015, 54, 21, 10243–10249; *Inorg. Chim. Acta* 2018, 480, 47–53; *Dalton Trans.*, 2016, 45, 13222-13233