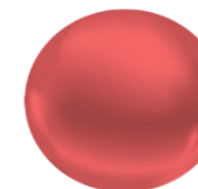
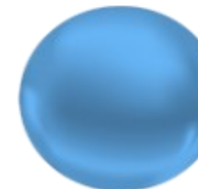


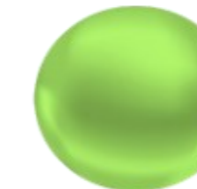
Franz Schmidt



Nikolaus Korber



Patrick Nürnberger



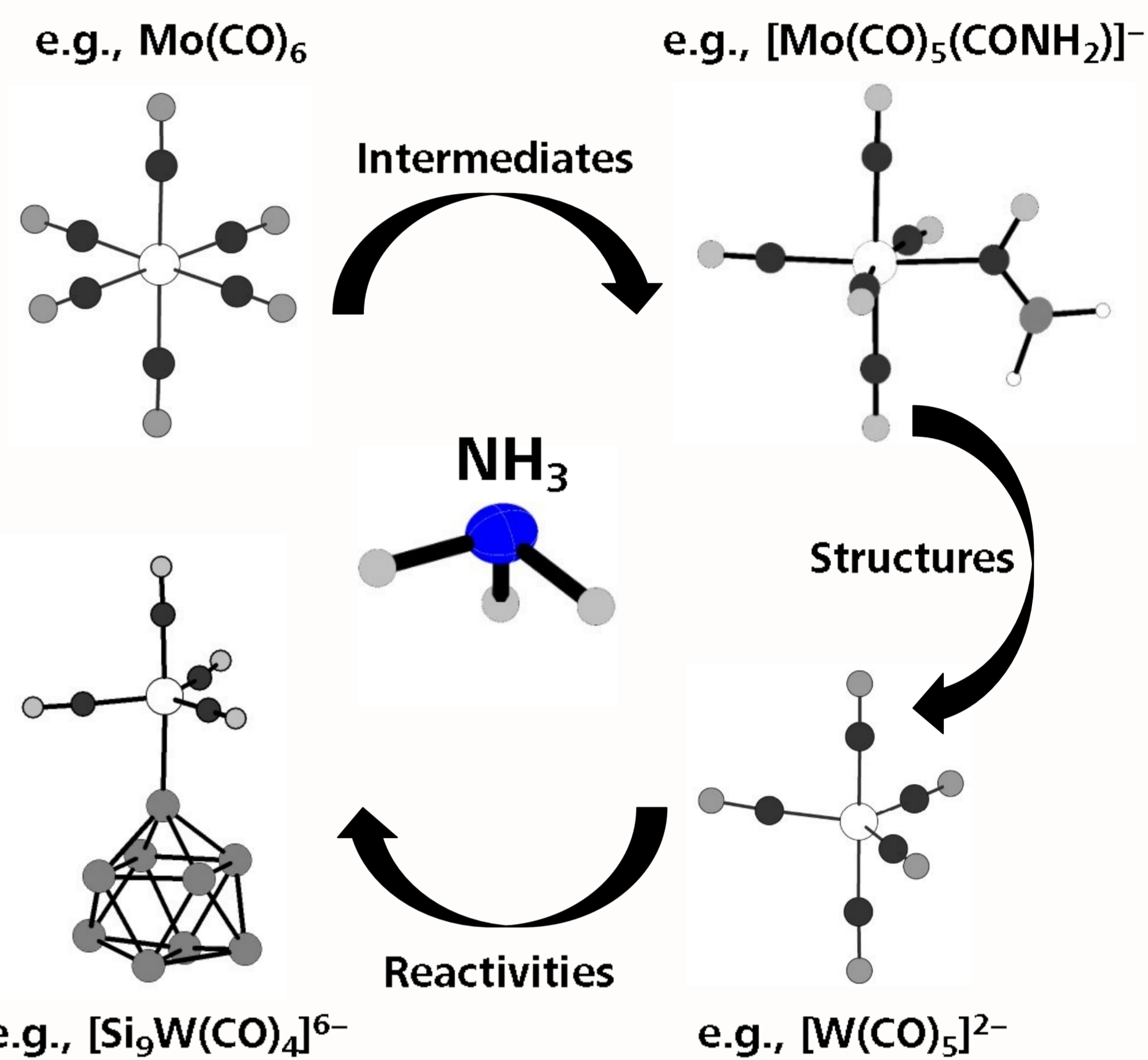
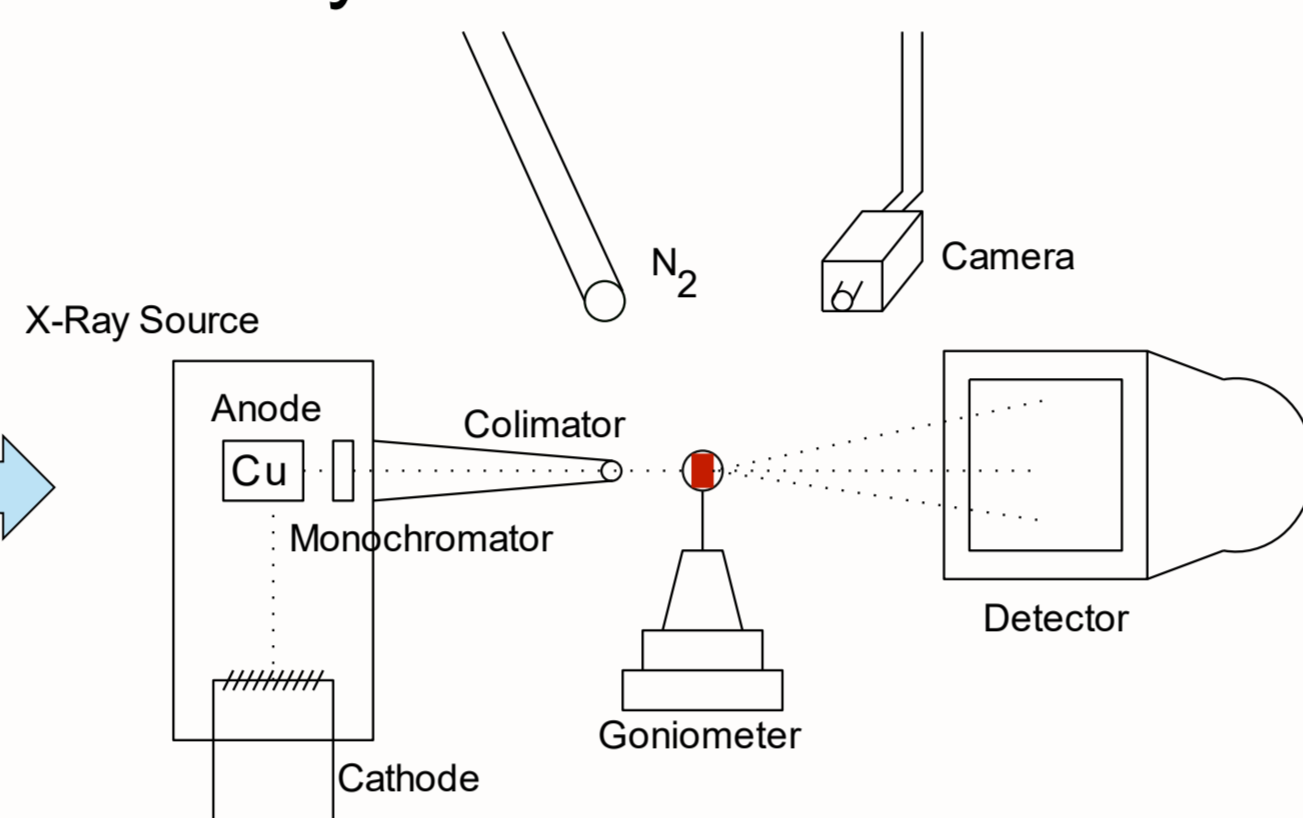
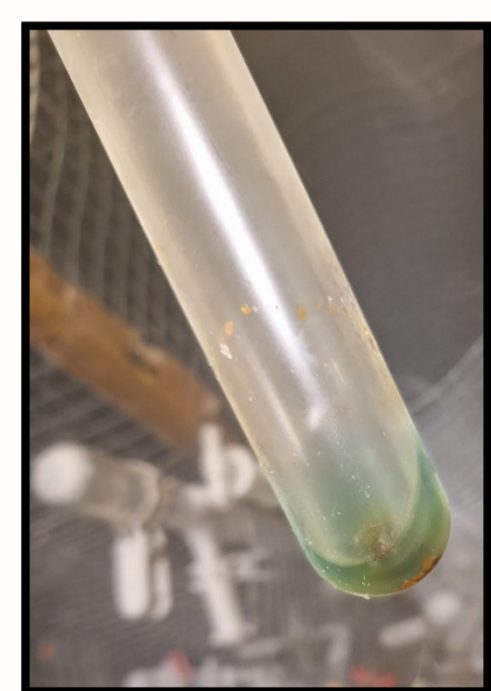
Robert Wolf



Department of Inorganic Chemistry, University of Regensburg

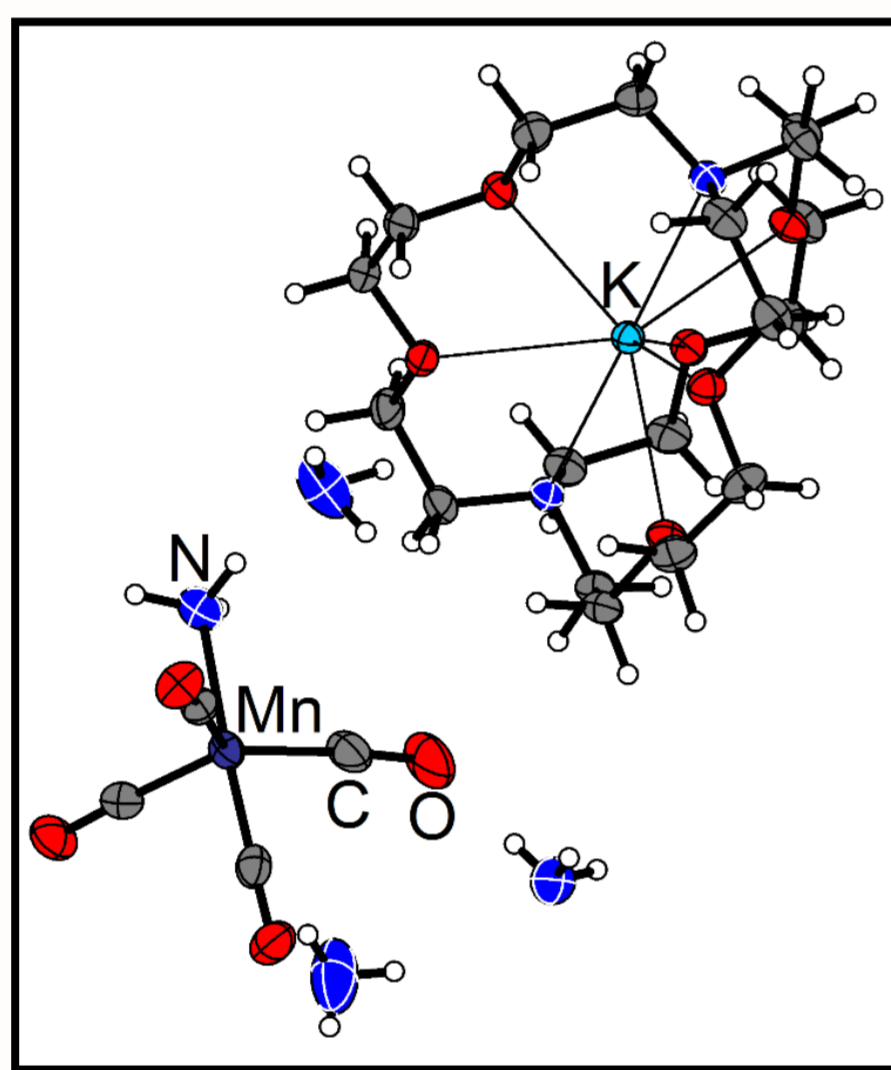
Abstract

Ion pairs of alkali metals with transition metal carbonylates can be generated by direct reduction of the neutral carbonyl complexes in liquid ammonia. The reduction is also possible when Zintl phases are used as reagents. From such solutions ammoniates of the respective carbonyl metalates are precipitating which can be analyzed by low temperature single crystal X-ray analysis. Often a dense network of ion pairs is observed in solid state. The reduction of carbonyl complexes is a suitable model system for in-depth structural study in solid state and solution.

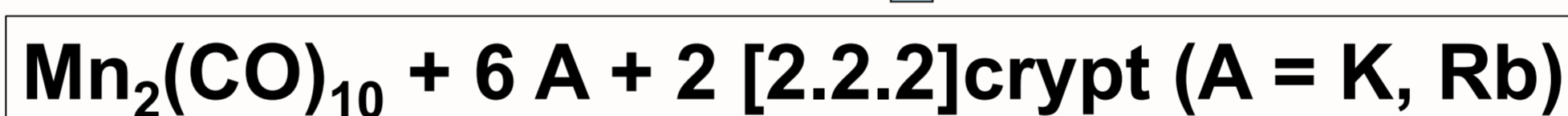
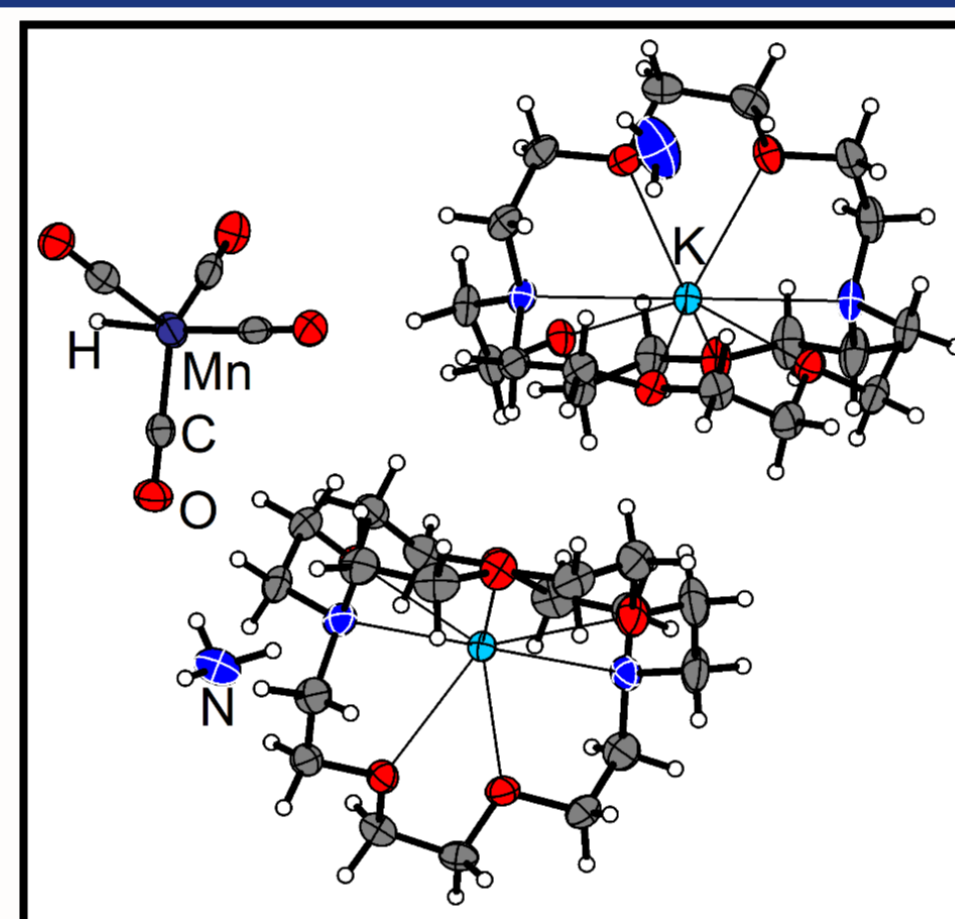
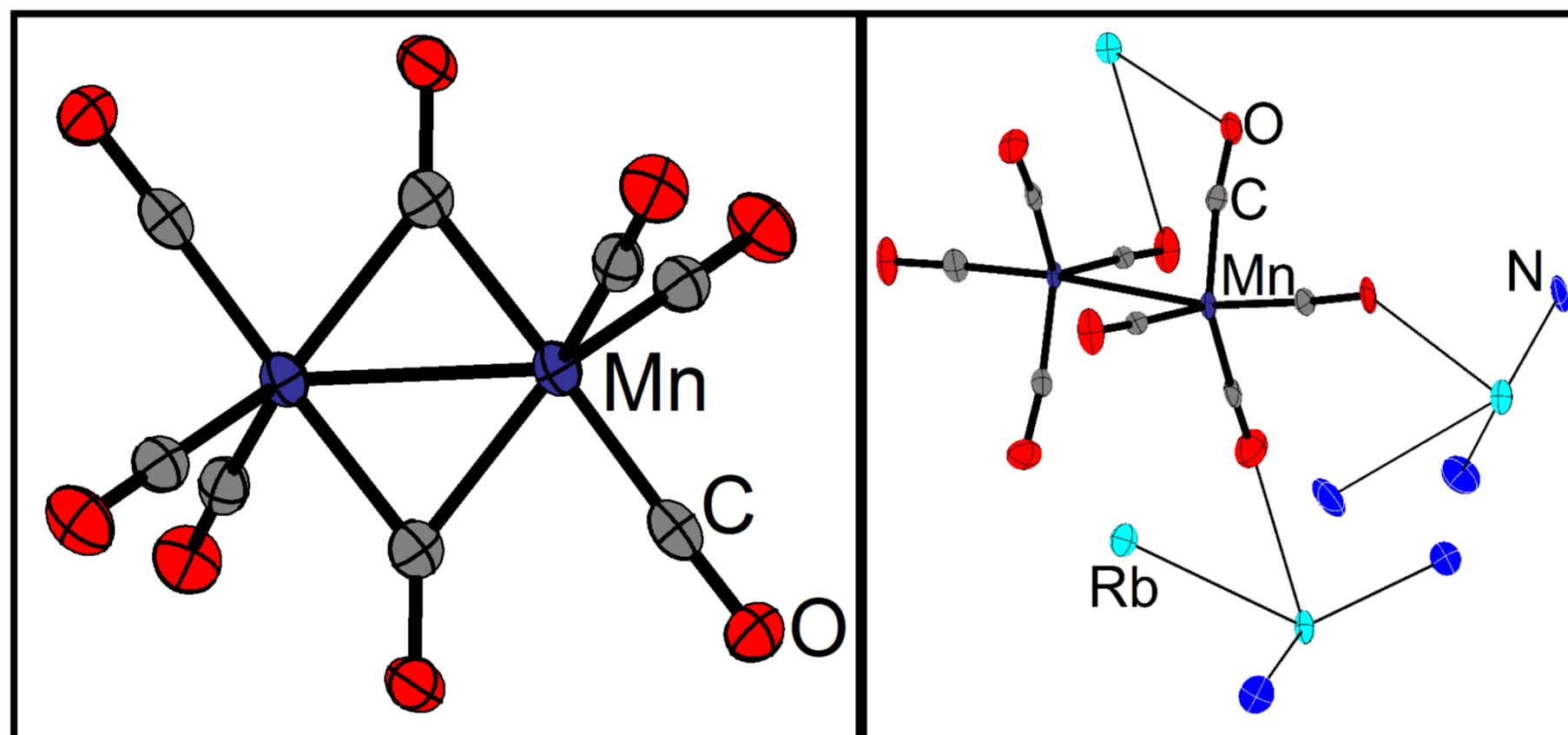


New Findings of Group 7 Carbonylates

- $[\text{Mn(CO)}_4(\text{NH}_3)]^-$ as intermediate in the reduction towards $[\text{Mn(CO)}_4]^{3-}$
- Coordination of the weaker π -acceptor NH_3 is driven by excess of ammonia

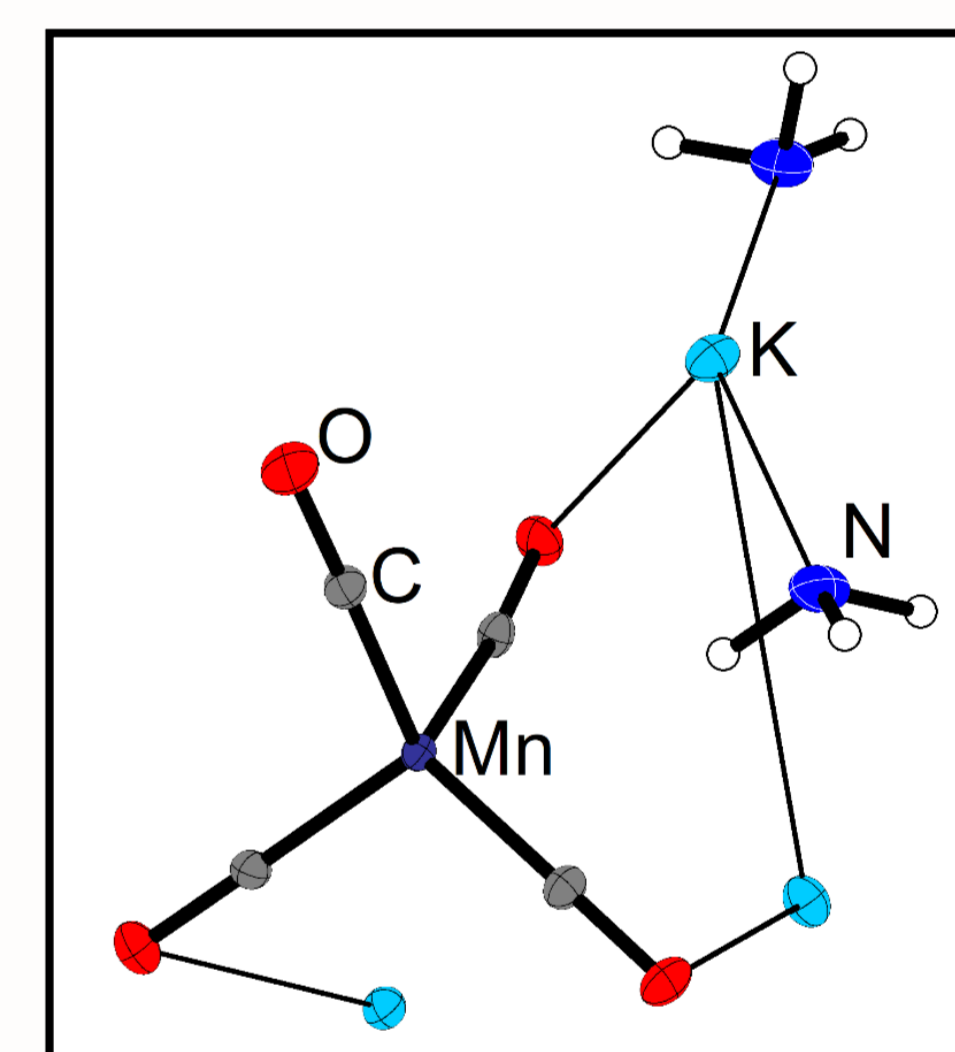


- Additionally, two dinuclear carbonylmanganates were observed from the reaction above
- The highly charged anions can be isolated due to multiple cation contacts in the crystal structure of the ammoniates



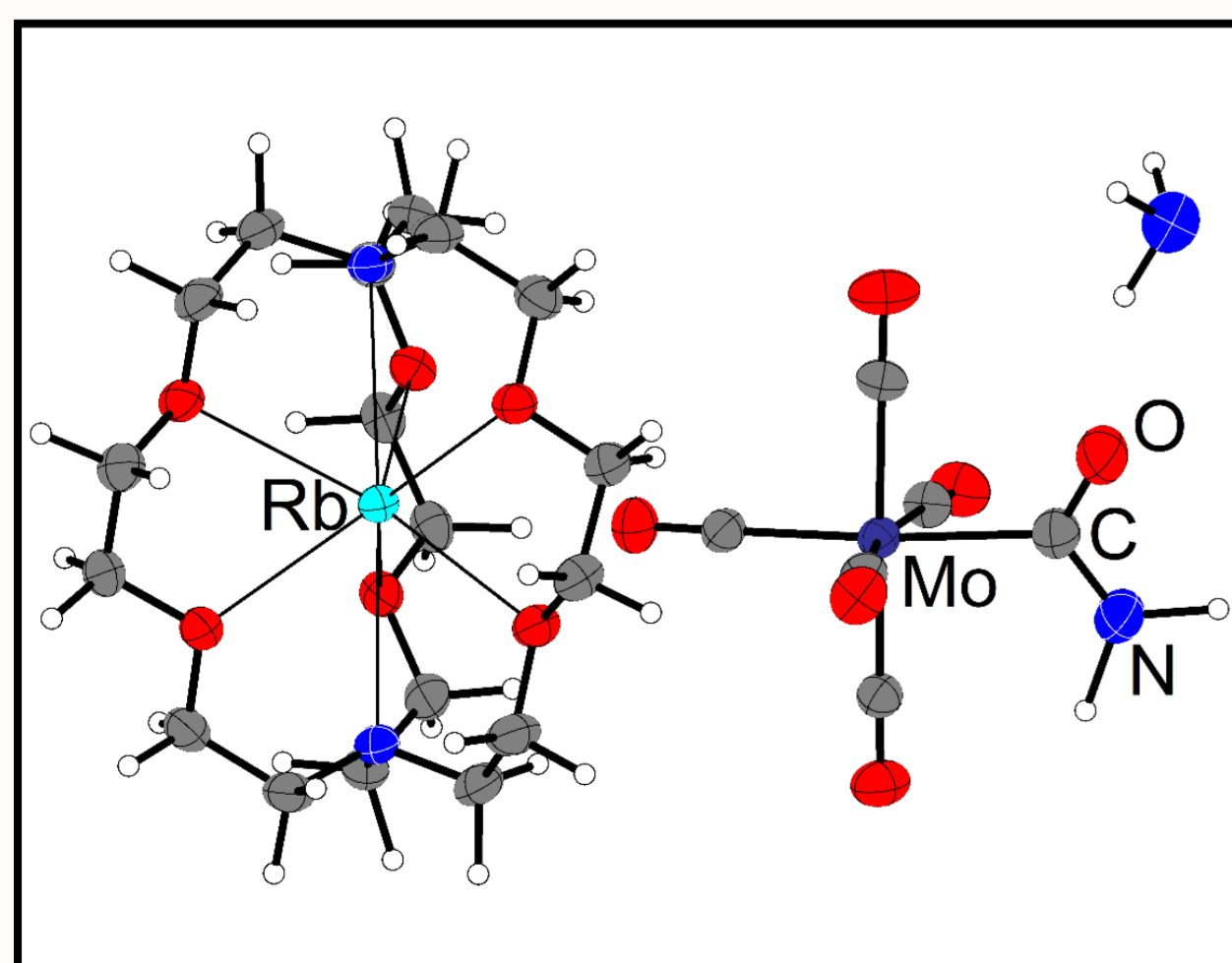
- Hydridic Carbonylmanganate(-III)
- The hydrogen atom is unequivocally in the crystal structure
- Isoelectronic to the first reported carbonylate $[\text{HFe(CO)}_4]^-$

- First crystal structure of $[\text{Mn(CO)}_4]^{3-}$
- Rhenium analogue found in $\text{K}_6[\text{Re(CO)}_4]_2 \cdot 7 \text{NH}_3$

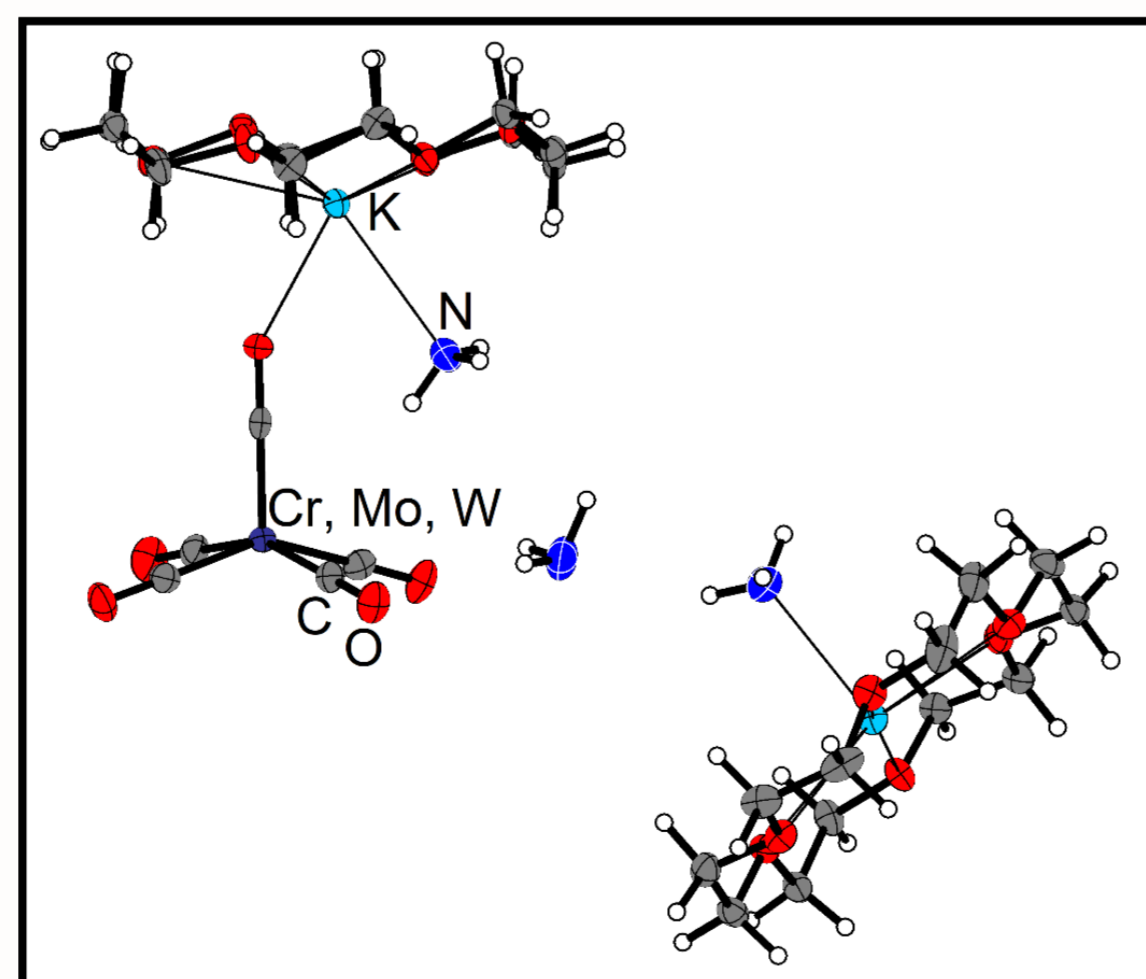


New Motifs of Group 6 Carbonylates

- $\text{Mo(CO)}_6 + \text{RbSnBi} + [2.2.2]\text{crypt}$
- Unusual Zintl phase reduction led to the formate intermediate $[\text{Mo(CO)}_5(\text{CONH}_2)]^-$ in group 6 metal carbonylate chemistry

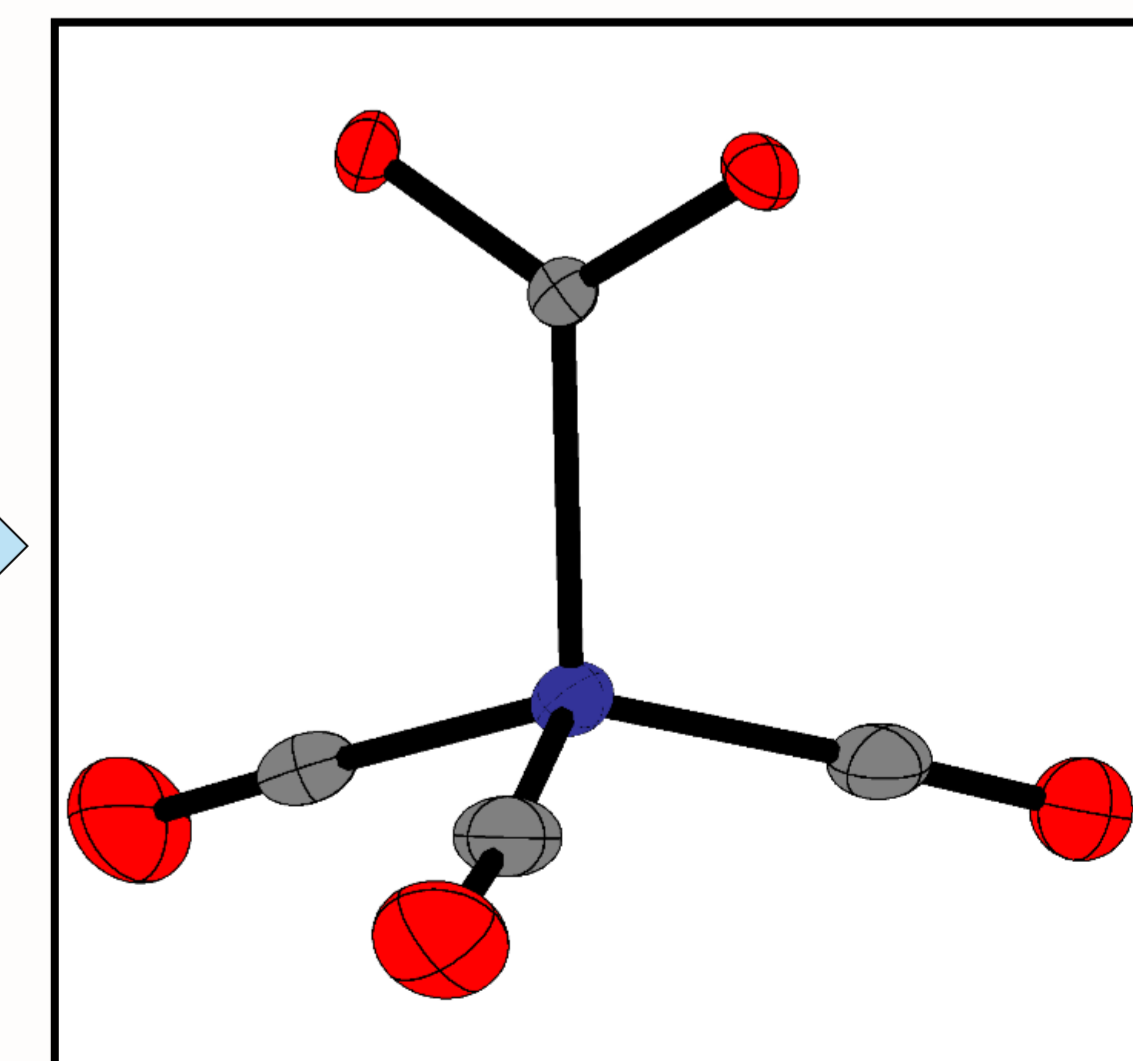
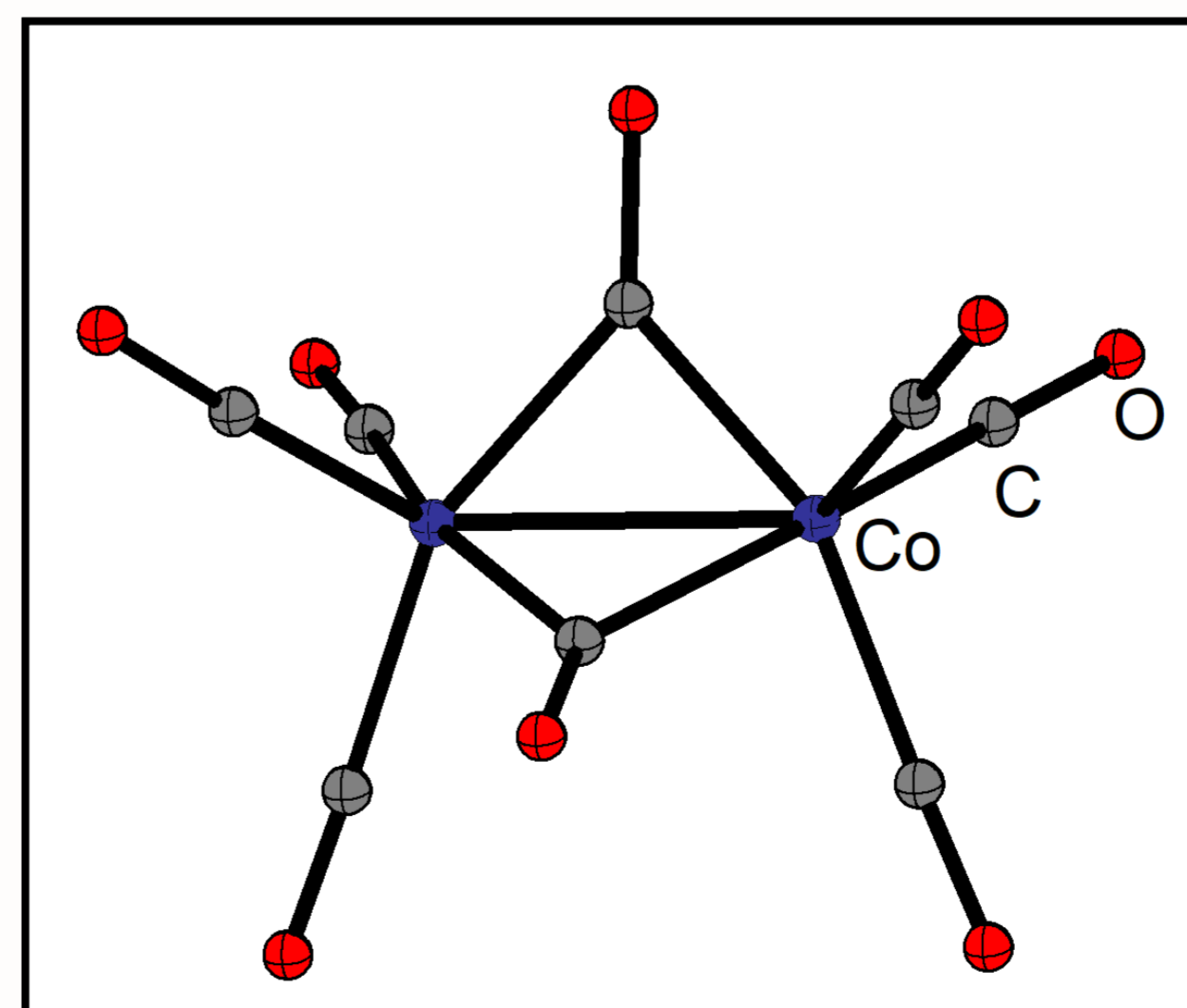


- Discovery of the square pyramidal pentacarbonylmetallate(-II)
- Use of 18crown-6 necessary for crystallization of this structural motif



Novel Group 9 Carbonylate

- Reaction of $\text{Co}_2(\text{CO})_8$ with rubidium led to the anion $[\text{Co(CO)}_3(\text{CO}_2)]^{3-}$
- CO_2 ligand coordinates in a carbene like fashion
- Coordination mode is comparable with $[\text{Fe,Ni}]\text{-CO-dehydrogenase}$



Connections within the RTG

P8 Prof. Dr. Patrick Nürnberger, Stephan Muth:
Vibrational spectroscopic studies of metal carbonylates in liquid ammonia

P6 Prof. Dr. Ruth Gschwind, Franz Westermair:
NMR measurements of metal carbonylates in liquid ammonia

Literature

- [1] J. E. Ellis, *Organomet.* **2003**, 22, 3322-3338.
- [2] W. Hieber, F. Leutert, *Z. Anorg. Allg. Chem.* **1932**, 204, 145-164.
- [3] G. F. P. Warnock, L. C. Moodie, J. E. Ellis, *J. Am. Chem. Soc.* **1989**, 111, 2131-2141.
- [4] G. G. Sumner, H. P. Klug, L. E. Alexander, *Acta Cryst.* **1964**, 17, 732-742.