

## VIII-D Syntheses, Structures, and Reactivities of Multinuclear Transition Metal Complexes with O- and N-Donor Ligands

Organotransition metal complexes with O- and N-donor ligands have recently been attracting considerable attention, because they often show structures, reactivities, and physicochemical properties significantly different from those of the complexes with P- and S-donor ligands. In this project it has been revealed that cyanamide ( $\text{NCN}^{2-}$ ) anion effectively bridge organometallic fragments to form multinuclear complexes with characteristic structures. It has recently been found that tetranuclear  $C_3$ -elongated cubane-like complexes of cobalt and rhodium can be synthesized from the reaction of  $[\text{Cp}^*\text{MX}_2]_2$  ( $M = \text{Co}, \text{Rh}; X = \text{Cl}, \text{I}$ ) with  $\text{Na}_2\text{NCN}$ . We have also investigated into the reactivities of coordinated NO in early and late heterobimetallic (ELHB) complexes and shown that the terminally bound NO ligand at a Rh-W bimetallic core undergoes unprecedented O-methylation.

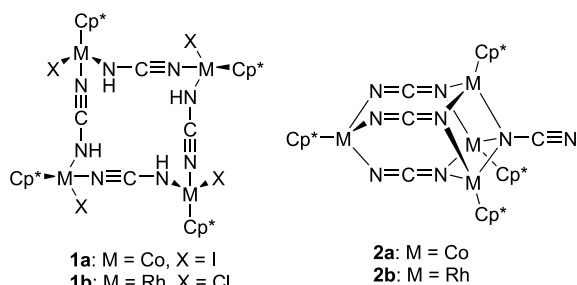
### VIII-D-1 Syntheses and Properties of NCN-Bridged Tri- and Tetranuclear Complexes of Cobalt and Rhodium

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The reaction of  $[\text{Cp}^*\text{CoI}_2]_2$  with 2 equiv of Na NCNH affords the 16-membered macrocyclic NCNH-bridged tetracobalt(III) complex  $[\text{Cp}^*\text{CoI}(\mu_2\text{-NCNH-}N,N')_4]$  (**1a**), while that with 2 equiv of  $\text{Na}_2\text{NCN}$  yields the  $C_3$ -elongated cubane-like NCN-bridged tetracobalt(III) complex  $[\text{Cp}^*\text{Co}(\mu_3\text{-NCN-}N,N,N')_3(\text{CoCp}^*)_3(\mu_3\text{-NCN-}N,N,N')]$  (**2a**). Treatment of  $[\text{Cp}^*\text{RhCl}_2]_2$  with 2 equiv of NaNCNH gives the  $C_3$ -elongated cubane-like tetrarhodium(III) complex  $[\text{Cp}^*\text{Rh}(\mu_3\text{-NCN-}N,N,N')_3(\text{RhCp}^*)_3(\mu_3\text{-NCN-}N,N,N')]$  (**2b**) via the macrocyclic complex  $[\text{Cp}^*\text{RhCl}(\mu_2\text{-NCNH-}N,N')_4]$  (**1b**) (Figure 1). On the other hand, the reaction of  $[\text{Cp}^*\text{CoCl}]_2$  with  $\text{Na}_2\text{NCN}$  affords the anionic bis(NCN)-capped tricobalt(II) complex  $\text{Na}[(\text{Cp}^*\text{Co})_3(\mu_3\text{-NCN-}N,N,N')_2]$ . The molecular structures of complexes **1a**· $\text{CH}_2\text{Cl}_2$  and **2b**· $2\text{C}_6\text{H}_6$  have been confirmed by X-ray analyses. The electrochemical properties of these types of NCN-bridged group 9 metal complexes have also been examined.



**Figure 1.** Structures of NCN-bridged Co and Rh tetranuclear complexes.

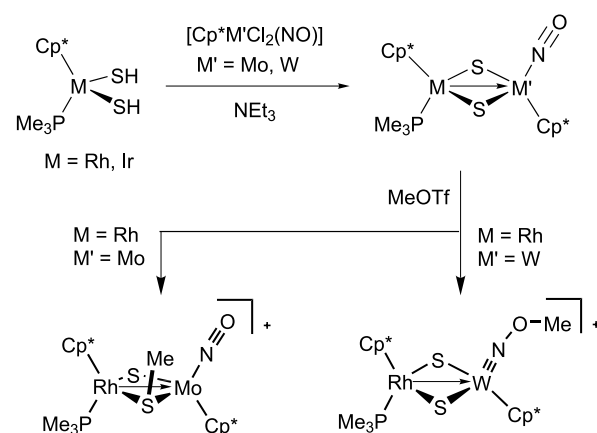
### VIII-D-2 Electrophilic O-Methylation of a Terminal Nitrosyl Ligand Attained by Early-Late Heterobimetallic Effect

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The reaction of the group 9 bis(hydrosulfido) complexes  $[\text{Cp}^*\text{M}(\text{SH})_2(\text{PMe}_3)]$  ( $M = \text{Rh}, \text{Ir}$ ) with the group 6 nitrosyl complexes  $[\text{Cp}^*\text{M}'\text{Cl}_2(\text{NO})]$  ( $M' = \text{Mo}, \text{W}$ ) in the presence of  $\text{NEt}_3$  affords a series of the bis(sulfido)-bridged early-late heterobimetallic (ELHB) complexes  $[\text{Cp}^*\text{M}(\text{PMe}_3)(\mu\text{-S})_2\text{M}'(\text{NO})\text{Cp}^*]$  ( $M = \text{Rh}, \text{Ir}; M' = \text{Mo}, \text{W}$ ). These complexes show one strong IR absorption assignable to the NO stretching around  $1500 \text{ cm}^{-1}$ . Interestingly, this  $\nu(\text{NO})$  value is  $100 \text{ cm}^{-1}$  smaller than that of the mononuclear thiolato complex  $[\text{Cp}^*\text{W}(\text{NO})(\text{SPh})_2]$ . This unusual IR absorption is attributable to the influx of electrons to the group 6 metal center through the  $M(\text{III}) \rightarrow M'(\text{II})$  dative bond. The electron rich nature of the dinuclear complexes is reflected in its reactivities. Upon treatment of the Rh–W complex with MeOTf, the oxygen atom of the terminal nitrosyl ligand is readily methylated to form the methoxyimido complex  $[\text{Cp}^*\text{Rh}(\text{PMe}_3)(\mu\text{-S})_2\text{W}(\text{NOMe})\text{Cp}^*]^+$ , while methylation of the Rh–Mo complex results in S-methylation, giving the methanethiolato complex  $[\text{Cp}^*\text{Rh}(\text{PMe}_3)(\mu\text{-SMe})(\mu\text{-S})\text{Mo}(\text{NO})\text{Cp}^*]^+$  (Scheme 1).



**Scheme 1.**