VIII-I Preparation and Properties of the Homo- and Heterometallic Clusters

This project focuses on the development of a systematic synthetic route to a series of the homo- and heterometallic clusters as templates or catalysts for new types of activation and transformation of organic, inorganic, and organometallic molecules at the well-defined multimetallic reaction sites. Especially, preparation and reactivity of dinuclear Ru(II) complexes having the bridging amido ligands has been extensively studied.

VIII-I-1 Reactivity of Amido Ligands on a Dinuclear Ru(II) Center: Formation of Imido Complexes and C-N Coupling Reaction with Alkyne

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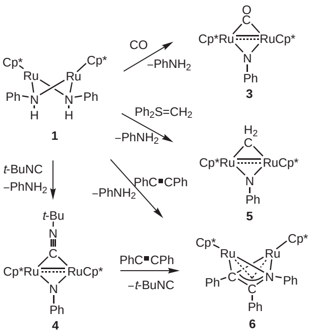
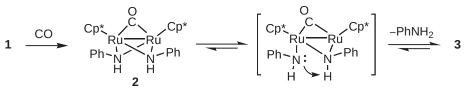
Reactions of the dimeric Ru(II) anilido complex $[Cp^*Ru(\mu_2\text{-}NHPh)]_2$ (**1**; Cp* = η^5-C_5Me_5) with CO, *t*-butyl isocyanide, a sulfur ylide $Ph_2S{=}CH_2$, and diphenylacetylene proceeded with an unexpected disproportionation of the μ_2-anilido ligands to form free aniline and a series of new imidodiruthenium complexes **3**–**5** (Scheme 1). In the case of diphenylacetylene, the imido fragment underwent subsequent coupling reaction with the alkyne to produce an iminoalkenyl complex **6**.





Existence of a Ru–Ru multiple bond is suggested by electron counting and the short Ru–Ru distance that is close to those of some other compounds with Ru=Ru double bonds (2.417–2.629 Å). Orbital analysis of a DFT-B3PW91 optimized model compound $[(CpRu)_2(\mu_2\text{-}CO)(\mu_2\text{-}NH)]$ (**3’**) has provided inshights into the Ru–Ru bond in **3**. Although the first six of HOMOs of **3’** are predominantly metal-based orbitals and constitute a formally nonbonded $\sigma^2\sigma^{*2}\delta^4\delta^{*4}$ configuration, the multiple bond order between the Ru atoms can be rationalized by back-donation from the filled Ru–Ru σ^* orbital into a π^* orbital of the CO ligand, and by donation from the imido and CO ligands into empty Ru–Ru π-bonding orbitals.

VIII-I-2 A Dinuclear Ru(II) Chelateing Amido Complex: Synthesis, Characterization, and Coupling Reaction with Carbon Monoxide

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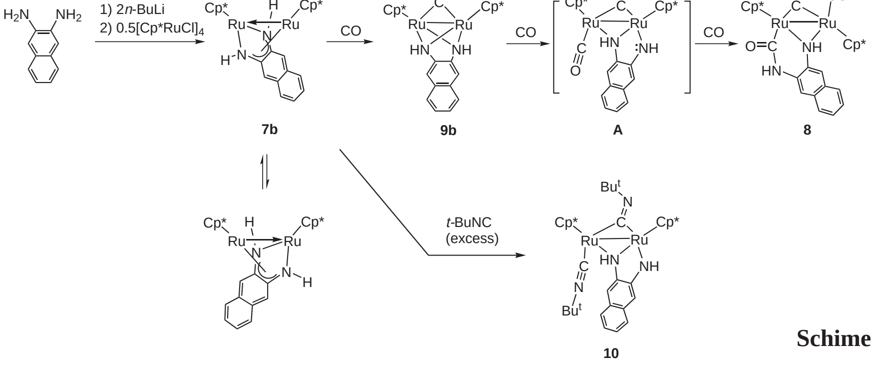
Results are summarized in Scheme 1. $[Cp^*RuCl]_4$ (Cp* = η^5-C_5Me_5) reacts with 2 equiv of dilithium 2,3-naphthalenediamide to afford a dinuclear bridging amido complex **7b** in moderate yield. Treatment of **7b** with CO (1 atm) resulted in the incorporation of three molecules of CO into the diruthenium core to give a carbamoyl amido bis(carbonyl) complex **8**. Similar treatment of **7b** with *tert*-butyl isocyanide resulted in the quantitative formation of a bis(isocyanide) complex **10**, in which the two amido nitrogen atoms also occupy the terminal and bridging coordination sites.



Schime 1.