

VIII-C 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, imido, and alkoxido ligands has been extensively studied.

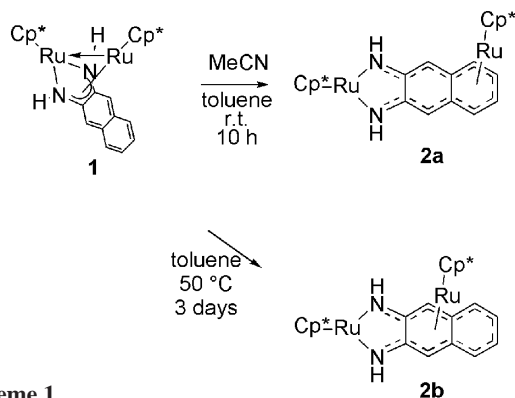
VIII-C-1 A Dinuclear Ru(II) κ^2 -Diamido/ η^6 -Naphthalene Complex Featuring a Coordinatively Unsaturated Yet Highly p -Basic (η^5 -C₅Me₅)Ru Diamide Fragment

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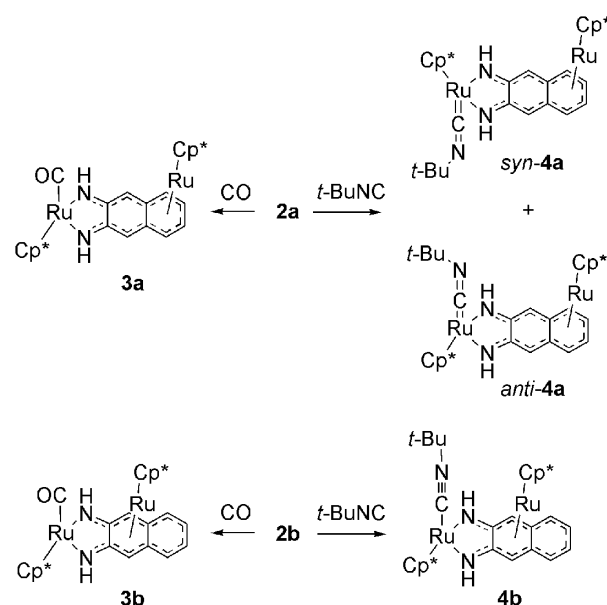
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Acetonitrile induced a clean isomerization of the amido-bridged diruthenium complex [(Cp*₂Ru)₂{ μ_2 - κ^2 : η^4 -2,3-naphthalenediamido}] (**1**) into a κ^2 : η^6 -bonded dinuclear complex [Cp*₂Ru{ μ^2 - κ^2 : η^6 -2,3-naphthalenediamido}RuCp*] (**2a**) featuring a coordinatively unsaturated Cp*₂Ru terminal diamide fragment. Isomerization of **1** also took place on heating a solution of **1** in hexanes, toluene, or toluene-acetone at 50 °C to give another isomer **2b** selectively, in which the {Cp*₂Ru}⁺ fragment is bound to the inner ring of the naphthalene moiety.



Scheme 1.

Structural and spectroscopic data of its carbon monoxide or *tert*-butyl isocyanide adducts indicated that the Cp*₂Ru diamide fragment can serve as a strong π -base.



Scheme 2.

VIII-C-2 Dinuclear Ruthenium(II) Catecholato and 2,3-Naphthalenediolato Complexes Featuring κ^2 -Diaryloxo/ η^6 -Arene Coordination Mode

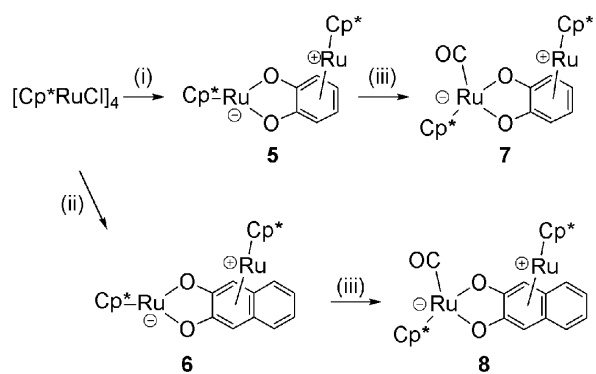
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A new dinuclear ruthenium(II) catecholato complex [Cp*₂Ru(κ^2 : η^6 - μ_2 -1,2-O₂C₆H₄)RuCp*] (**5**; Cp* = η^5 -C₅Me₅) has been prepared by the reaction of [Cp*₂RuCl]₄ with 2 equiv of disodium catecholate in THF. Complex **5** has a dinuclear structure, in which one of the Cp*₂Ru fragments is κ^2 -bonded to the two oxygen atoms and the other is η^6 -bonded to the aromatic ring. Similar treatment of [Cp*₂RuCl]₄ with disodium 2,3-naphthalenediolate affords an analogous κ^2 : η^6 -bonded dinuclear complex [Cp*₂Ru(κ^2 : η^6 - μ_2 -2,3-O₂C₁₀H₆)RuCp*] (**6**) with selective π -complexation at the oxygen-substituted naphthalene ring. The molecular structure of **6** has been determined by X-ray crystallography. The oxygen-bound ruthenium atoms in complexes **5** and **6** are coordinatively unsaturated and readily uptake 1 equiv of carbon monoxide to give the corresponding carbonyl adducts [Cp*₂Ru(CO)(κ^2 : η^6 - μ_2 -1,2-O₂C₆H₄)RuCp*] (**7**)

and $[\text{Cp}^*\text{Ru}(\text{CO})(\kappa^2:\eta^6-\mu_2-2,3-\text{O}_2\text{C}_{10}\text{H}_6)\text{RuCp}^*]$ (**8**), respectively.



Scheme 1. Preparation of Complexes. (i) $\text{Na}_2[1,2-\text{O}_2\text{C}_6\text{H}_4]$, (ii) $\text{Na}_2[2,3-\text{O}_2\text{C}_{10}\text{H}_6]$, (iii) CO (1 atm).