

# Hydrocarbon Ligand Derivative Chemistry of the Dicarbido Decaruthenium Framework

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Final Seminar

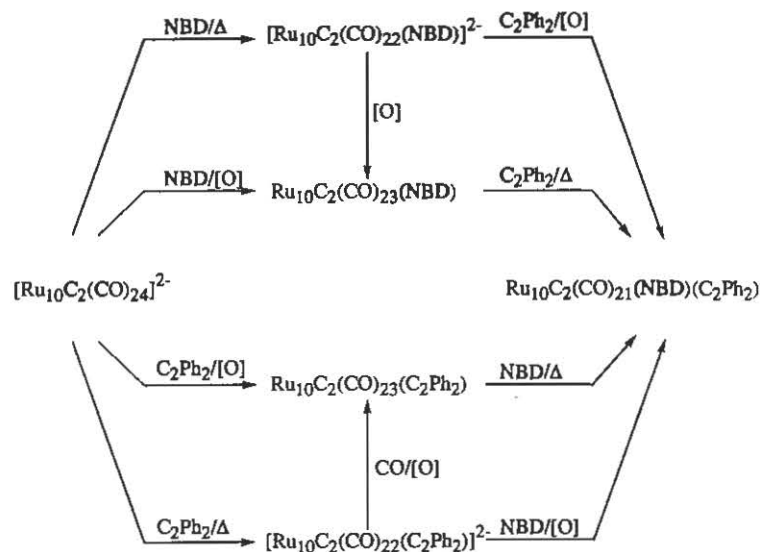
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Only a few higher nuclearity cluster systems have been examined for systematic hydrocarbon ligand chemistry, with most known derivatives based on the octahedral  $Ru_6(\mu_6-C)$  framework.<sup>1,2</sup> The decaruthenium cluster  $[Ru_{10}C_2(CO)_{24}]^{2-}$  has a structure that can be viewed as two  $Ru_6C$  octahedra sharing a common edge.<sup>3</sup> This partial fusion of subunits creates a new type of substitution site, an 'inner' site at or near the area of fusion, which contrasts with the typical type of 'outer' site on the convex surface of the cluster frame. Previous workers in our group have shown that  $[Ru_{10}C_2(CO)_{24}]^{2-}$  undergoes substitution with diphenylacetylene at

125 °C to form  $[Ru_{10}C_2(CO)_{22}(C_2Ph_2)]^{2-}$ ,<sup>4a</sup> in which the alkyne ligand is in an 'inner' position bridging an apical-apical Ru-Ru bond. The substitution is reversed under a carbon monoxide atmosphere at 125 °C, which is a testament to the robust nature of the  $Ru_{10}C_2$  framework. To further explore the reactivity of  $[Ru_{10}C_2(CO)_{24}]^{2-}$ , we have examined its interaction with various hydrocarbon ligands, namely, allene, norbornadiene, alkynes, and  $C_{60}$ .

The reaction of  $[Ru_{10}C_2(CO)_{24}]^{2-}$  with allene in diglyme at 90 °C provides a monoallene derivative  $[Ru_{10}C_2(CO)_{22}(CH_2CCH_2)]^{2-}$ , which displays substitution at an inner, bridging site. Furthermore, reaction with allene at 140 °C gives an analogous diallene derivative,  $[Ru_{10}C_2(CO)_{20}(CH_2CCH_2)_2]^{2-}$ . Both allene ligands can be removed under CO pressure.

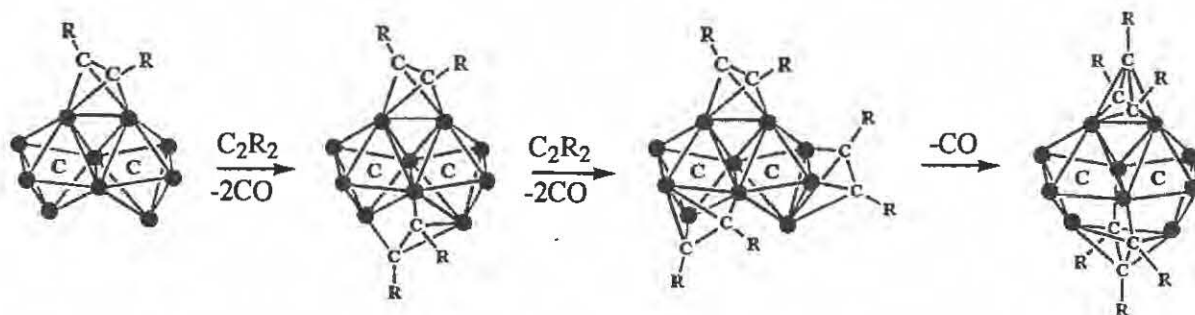
The reaction of  $[Ru_{10}C_2(CO)_{24}]^{2-}$  with norbornadiene (NBD) in diglyme at 140 °C provides the anionic derivative  $[Ru_{10}C_2(CO)_{22}(NBD)]^{2-}$ . Oxidation of this compound with  $[Cp_2Fe][BF_4]$  affords the neutral derivative  $Ru_{10}C_2(CO)_{23}(NBD)$ , which can also be prepared by direct oxidative substitution of  $[Ru_{10}C_2(CO)_{24}]^{2-}$  with  $2[Cp_2Fe][BF_4]$  in the presence of NBD. Spectroscopic and crystallographic studies on  $[Ru_{10}C_2(CO)_{22}(NBD)]^{2-}$  and  $Ru_{10}C_2(CO)_{23}(NBD)$  show that the NBD ligand occupies a chelating position on one of the 'outer' ruthenium atoms in the bifurcated  $Ru_{10}C_2$  framework. Since this location contrasts with that adopted by the alkyne ligand in  $Ru_{10}C_2(CO)_{23}(C_2Ph_2)$ ,<sup>4b</sup> the generality of these substitution sites has been probed by preparing the mixed ligand derivative  $Ru_{10}C_2(CO)_{21}(NBD)(C_2Ph_2)$ . This compound can be synthesized in four distinct ways (see Scheme I): (1) by oxidation of



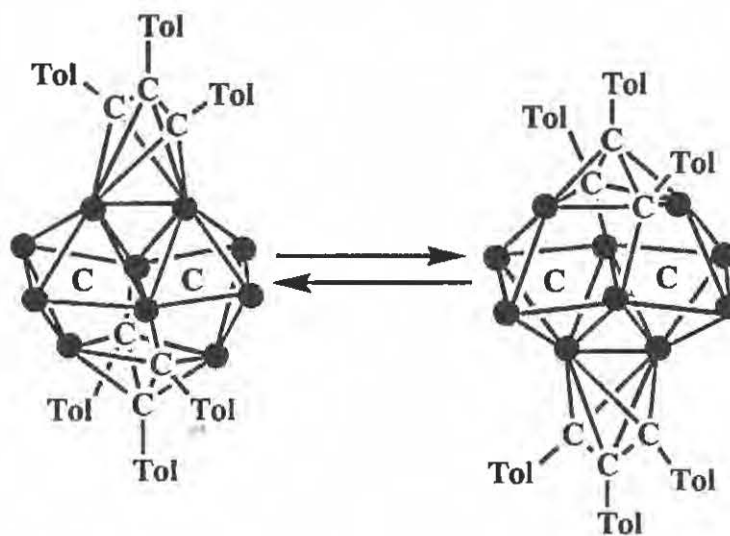
Scheme I

[Ru<sub>10</sub>C<sub>2</sub>(CO)<sub>22</sub>(NBD)]<sup>2-</sup> with 2[Cp<sub>2</sub>Fe][BF<sub>4</sub>] in the presence of C<sub>2</sub>R<sub>2</sub>; (2) by oxidation of [Ru<sub>10</sub>C<sub>2</sub>(CO)<sub>22</sub>(C<sub>2</sub>Ph<sub>2</sub>)]<sup>2-</sup> with 2[Cp<sub>2</sub>Fe][BF<sub>4</sub>] in the presence of NBD; (3) by thermal substitution of two carbonyl ligands in [Ru<sub>10</sub>C<sub>2</sub>(CO)<sub>23</sub>(NBD)] by C<sub>2</sub>R<sub>2</sub> in refluxing toluene; (4) by thermal substitution of two carbonyl ligands in Ru<sub>10</sub>C<sub>2</sub>(CO)<sub>23</sub>(C<sub>2</sub>Ph<sub>2</sub>) by NBD in refluxing toluene. The substitution sites observed for the individual ligands are maintained in the mixed ligand derivative.

Substitution of two carbonyl ligands in Ru<sub>10</sub>C<sub>2</sub>(CO)<sub>23</sub>(C<sub>2</sub>R<sub>2</sub>) (R = Ph, Tol)<sup>4b</sup> by C<sub>2</sub>R'<sub>2</sub> (R' = Ph, Tol) in refluxing toluene affords the dialkyne derivative Ru<sub>10</sub>C<sub>2</sub>(CO)<sub>21</sub>(C<sub>2</sub>R<sub>2</sub>)(C<sub>2</sub>R'<sub>2</sub>) (R, R' = Ph, Tol). The two alkyne ligands are both bound in inner positions but differ in bonding mode, namely, μ-η<sup>2</sup>:η<sup>2</sup> and μ<sub>3</sub>-η<sup>1</sup>:η<sup>1</sup>:η<sup>2</sup>. In solution they interchange their bonding modes concomitant with flexing of the metal framework. Extended treatment of Ru<sub>10</sub>C<sub>2</sub>(CO)<sub>21</sub>(C<sub>2</sub>Tol<sub>2</sub>)<sub>2</sub> with C<sub>2</sub>Tol<sub>2</sub> in refluxing octane forms the trialkyne derivative Ru<sub>10</sub>C<sub>2</sub>(CO)<sub>19</sub>(C<sub>2</sub>Tol<sub>2</sub>)<sub>3</sub> with one μ-η<sup>2</sup>:η<sup>2</sup> alkyne ligand and two μ<sub>3</sub>-η<sup>1</sup>:η<sup>1</sup>:η<sup>2</sup> alkyne ligands. Pyrolysis of this trialkyne complex gives the bis(dimetallaallyl) derivative Ru<sub>10</sub>C<sub>2</sub>(CO)<sub>18</sub>(C<sub>3</sub>Tol<sub>3</sub>)<sub>2</sub> with dimetallaallyl ligands displaying μ-η<sup>3</sup>:η<sup>3</sup> and μ<sub>4</sub>-η<sup>1</sup>:η<sup>3</sup>:η<sup>3</sup>:η<sup>1</sup> bonding modes (see Scheme II). In solution these two ligands interchange their bonding modes along with major Ru-Ru bond making and breaking (see Scheme III).



Scheme II



Scheme III

Finally, treatment of  $[\text{Ru}_{10}\text{C}_2(\text{CO})_{24}]^{2-}$  with  $\text{C}_{60}$  in chlorobenzene/diglyme (1/4) at  $130\text{ }^\circ\text{C}$  forms  $[\text{Ru}_{10}\text{C}_2(\text{CO})_{22}(\text{C}_{60})]^{2-}$ . The  $^{13}\text{C}$  NMR study of  $^{13}\text{C}$  enriched  $[\text{Ru}_{10}\text{C}_2(\text{CO})_{22}(\text{C}_{60})]^{2-}$  suggests that the  $\text{C}_{60}$  ligand bridges two apical ruthenium atoms in the  $\mu\text{-}\eta^2\text{:}\eta^2$  bonding mode which has been observed for some smaller complexes.<sup>5</sup>

## References

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