

## The Chemistry of Triruthenium Hydrocarbyls

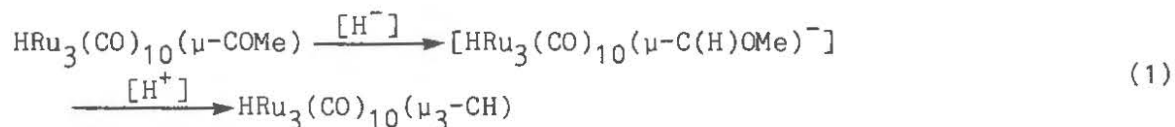
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Final Seminar

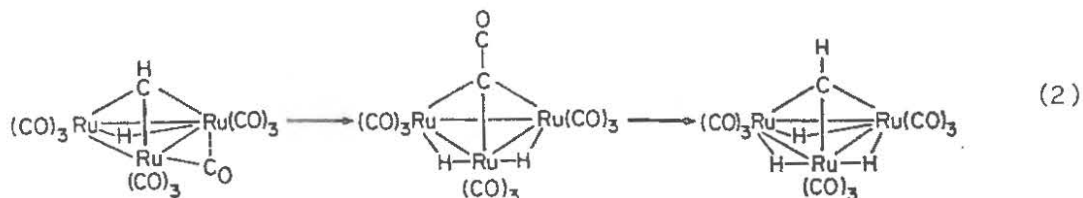
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Scientists seeking to improve the reactivity and selectivity of CO-hydrogenolysis catalysts may benefit from an improved mechanistic understanding of surface processes. The complexity of these catalytic processes and the difficulties inherent in examining surface reactions, however, has forced researchers to study polynuclear transition metal compounds. Such compounds feature adjacent metal sites and hence serve as useful models for metal surfaces [1]. Recent studies have focused on the synthesis and characterization of key ligand types including cluster-bound alkyl, alkylidene and alkylidyne groups [2]. We have sought an improved understanding of the interconversion and coupling of such ligands through the use of labile triruthenium hydrocarbyl clusters.

The methoxy-substituted carbyne cluster,  $\text{HRu}_3(\text{CO})_{10}(\mu\text{-COCH}_3)$  [3], provides a readily accessible route to the triruthenium methylidyne cluster,  $\text{HRu}_3(\text{CO})_{10}(\mu_3\text{-CH})$  (reaction 1) [4].

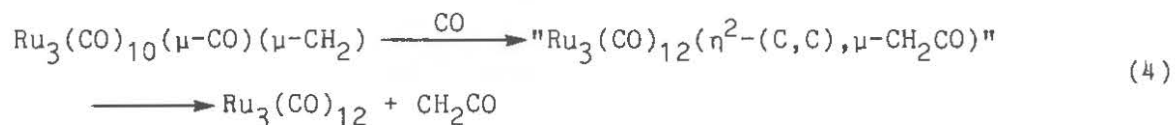
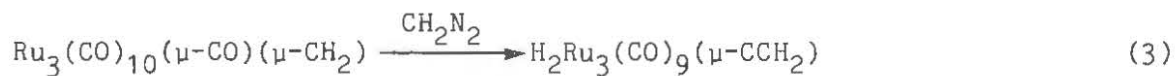


Variable temperature  $^1\text{H}$  and  $^{13}\text{C}$  NMR experiments suggest the intermediacy of a formyl complex, presumably  $[\text{HRu}_3(\text{CO})_9(\text{C(H)O})(\mu\text{-COCH}_3)^-]$ , in the preparation of  $\text{HRu}_3(\text{CO})_{10}(\mu_3\text{-CH})$ . The methylidyne cluster,  $\text{HRu}_3(\text{CO})_{10}(\mu_3\text{-CH})$ , rearranges rapidly ( $-10^\circ\text{C}$ ) to the isomeric carbonylmethylidyne cluster,  $\text{H}_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-CCO})$ , via intramolecular coupling of the carbyne ligand and a cluster-bound carbonyl. Hydrogenation of  $\text{H}_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-CCO})$  yields  $\text{H}_3\text{Ru}_3(\text{CO})_9(\mu_3\text{-CH})$  [3], demonstrating that this C-C coupling process is reversible (reaction 2)



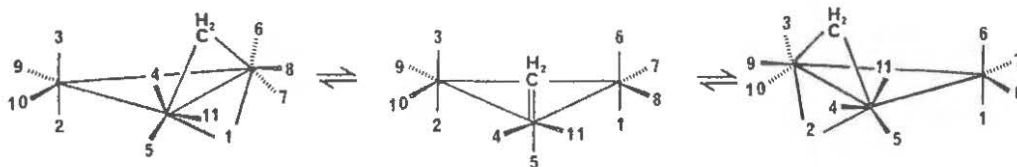
The carbonylmethylidyne cluster,  $\text{H}_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-CCO})$ , is reduced to the vinylidene cluster,  $\text{H}_2\text{Ru}_3(\text{CO})_9(\mu\text{-CCH}_2)$  [5], with  $\text{BH}_3 \cdot \text{THF}$ . This reduction is particularly noteworthy as it points to the possibility of isolating hydrocarbons, not just oxygenated products, from chain growth processes involving intact CO.

The triruthenium methylene cluster,  $\text{Ru}_3(\text{CO})_{10}(\mu\text{-CO})(\mu\text{-CH}_2)$ , is prepared by the reaction of diazomethane and  $\text{Ru}_3(\text{CO})_{12}$  [6]. Reactivity studies point to facile C-C bond formation involving the cluster bound methylene and added diazomethane or added CO (reactions 3 and 4). The methylene cluster,  $\text{Ru}_3(\text{CO})_{10}(\mu\text{-CO})(\mu\text{-CH}_2)$ , thermally rearranges to the carbonylmethylidyne cluster,  $\text{H}_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-CCO})$ . This rearrangement probably involves the previously discussed methylidyne cluster,  $\text{HRu}_3(\text{CO})_{10}(\mu_3\text{-CH})$ .

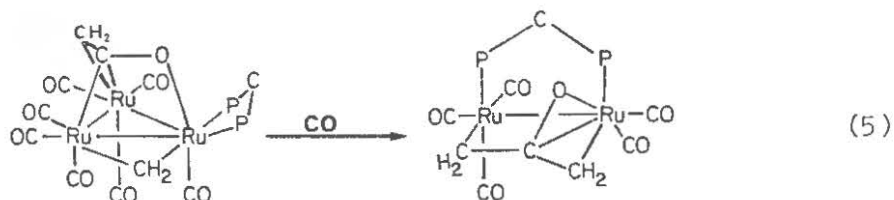


The mobility of surface-bound ligands has received a great deal of attention in recent years due to the proposed importance of such rearrangements to catalytic processes [7]. Spin saturation transfer experiments on  $\text{Ru}_3(\text{CO})_{10}(\mu\text{-CO})(\mu\text{-CH}_2)$  suggest that the methylene unit can move over the cluster face, presumably via a bridge-to-terminal isomerization process (Scheme 1). This is the first example supporting such an isomerization process for a cluster bound alkylidene ligand.

Scheme 1



Reaction of diazomethane with the phosphine substituted triruthenium cluster,  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$  [8], yields the novel cluster,  $\text{Ru}_3(\text{CO})_7(\eta^3\text{-C}_2\text{C}_2\text{O})(\mu_3\text{-COCH}_2)(\mu\text{-CH}_2)(\text{dppm})$  [9]. This cluster was characterized spectroscopically as well as by a single crystal X-ray diffraction study. The cluster contains a ketene ligand and a bridging methylene ligand. Surprisingly, each of the three atoms in the C-C-O unit, the ketene ligand, is bound to a different metal atom in the cluster. On addition of CO, the ketene and methylene ligands in  $\text{Ru}_3(\text{CO})_7(\eta^3\text{-C}_2\text{C}_2\text{O})(\mu_3\text{-COCH}_2)(\mu\text{-CH}_2)(\text{dppm})$  couple to form an oxoallyl unit while the triruthenium cluster degrades to a ruthenium dimer,  $\text{Ru}_2(\text{CO})_5(\eta^4\text{-C}_2\text{C}_2\text{C}_2\text{O})(\mu\text{-CH}_2\text{C}(\text{O})\text{CH}_2)(\text{dppm})$  (reaction 5), which was characterized by single crystal X-ray diffraction.



## References

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