

Synthesis and Reactivity of Cluster Bound Acetylides

Nam H. Hur

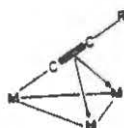
Literature Seminar

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There has been a great deal of study on the synthesis, bonding, structure, and reactivity of the alkyne transition metal complexes [1]. In particular, cluster bound acetylides ($\text{RC}\equiv\text{C}-$) have recently provided some interesting chemistry. The acetylide, which is related to $\text{C}\equiv\text{O}$ and $\text{C}\equiv\text{N}$ in its coordination chemistry, has a variety of bonding modes (e.g., $\mu-\eta^2$, $\mu_3-\eta^2$, $\mu_4-\eta^2$) in clusters. The interaction of the acety-



$\mu-\eta^2$



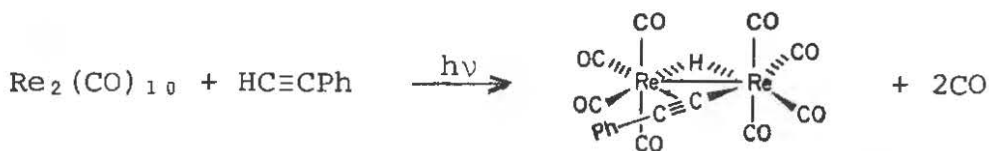
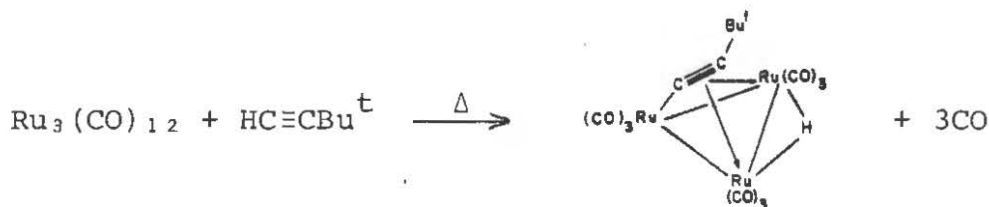
$\mu_3-\eta^2$



$\mu_4-\eta^2$

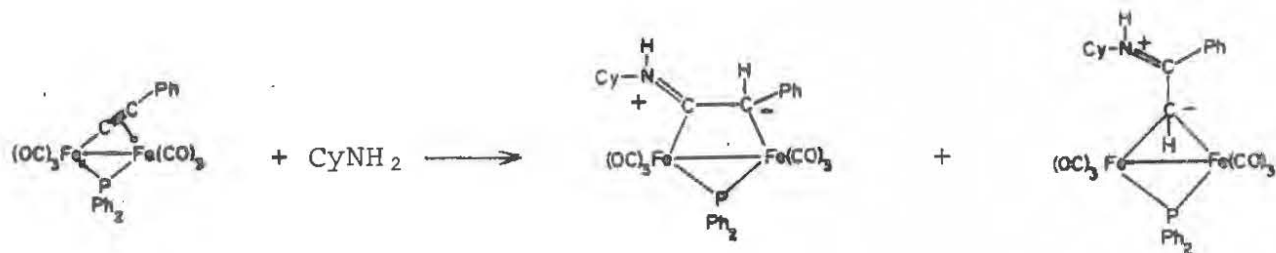
lide with metal atoms reveal unusual and possibly useful patterns of chemical reactivity.

The acetylide complexes are synthesized by substitution of carbonyl groups in metal carbonyl clusters with alkynes [2]. The carbonyl substitution reaction proceeds thermally or in the presence of Me_3NO in most cases and photochemically in a few cases. Thermal reaction of $\text{Ru}_3(\text{CO})_{12}$ with $\text{HC}\equiv\text{CBu}^t$ produces $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3-\eta^2\text{-C}\equiv\text{CBu}^t)$ [3]. Dirhenium decacarbonyl $\text{Re}_2(\text{CO})_{10}$ reacts photochemically with $\text{HC}\equiv\text{CPh}$ to yield $(\mu\text{-H})\text{Re}_2(\text{CO})_8(\mu-\eta^2\text{-C}\equiv\text{CPh})$ [4].

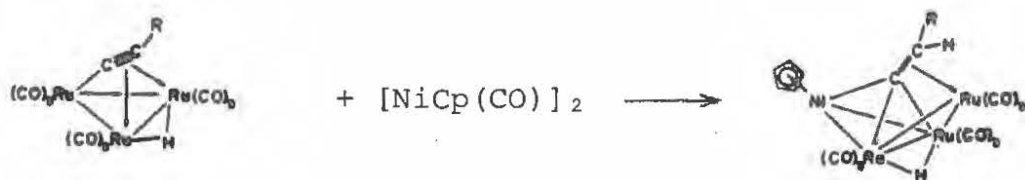


The reactivity of acetylide complexes has been studied with a variety of nucleophiles and electrophiles. Isomerization and hydrogenation have also been investigated.

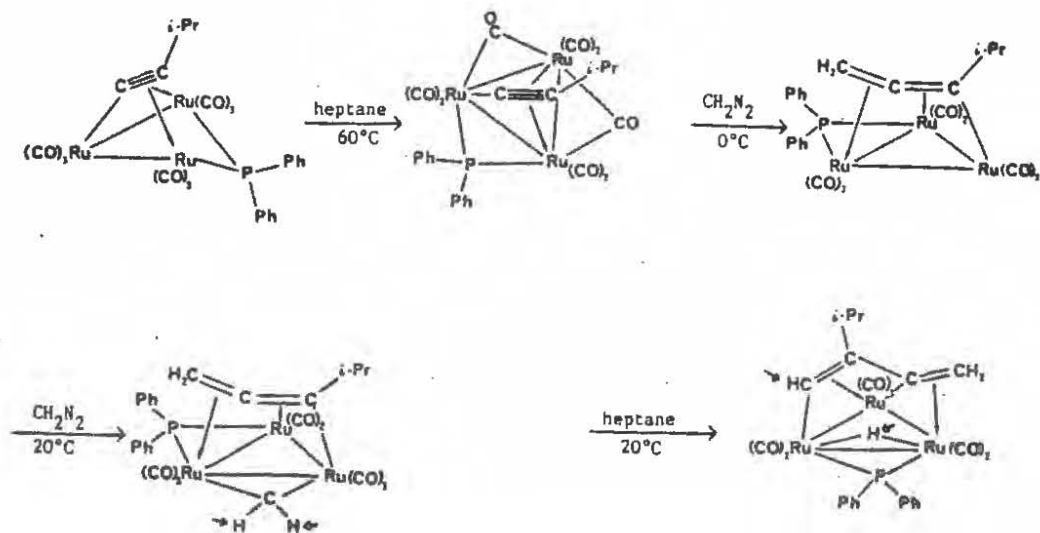
The nucleophilic reactions of $\mu\text{-}\eta^2$ acetylide $(\mu\text{-pph}_2)\text{Fe}_2(\text{CO})_6\text{-}(\mu\text{-}\eta^2\text{-C}\equiv\text{CPh})$ with amines, phosphines, phosphites, and isonitriles give adducts which have zwitterionic structures with the nucleophilic atoms attached to the original α - or β acetylenic carbon [5].



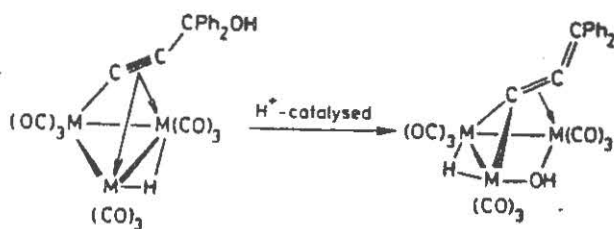
The $\mu_3\text{-}\eta^2$ acetylides $(\mu\text{-pph}_2)\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}\equiv\text{CPh})$ and $(\mu\text{-H})\text{Ru}_3(\text{CO})_9\text{-}(\mu_3\text{-}\eta^2\text{-C}\equiv\text{CPh})$ also react with nucleophiles [6]. The regioselectivity of nucleophilic attack depends on the electronic and steric properties of the group R and incoming nucleophiles. Under certain conditions, nucleophilic attack causes carbonyl substitution. For $(\mu\text{-H})\text{Ru}_3(\text{CO})_9\text{-}(\mu_3\text{-}\eta^2\text{-C}\equiv\text{C}^t\text{Bu})$, reactions with phosphites and phosphines yield only substitution products of the type $(\mu\text{-H})\text{Ru}_3(\text{CO})_8(\mu_3\text{-}\eta^2\text{-C}\equiv\text{C}^t\text{Bu})(\text{L})$ [7]. Carbonyl substitution occurs regioselectively on the ruthenium atom σ bonded to the acetylide. The metallic nucleophile such as $[\text{NiCp}(\text{CO})]_2$ reacts with $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}\equiv\text{C}^i\text{Pr})$ to yield a mixed metal vinylidene cluster $(\mu\text{-H})(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{Ru}_3(\text{CO})_9(\mu_4\text{-}\eta^2\text{-C}=\text{CH}^i\text{Pr})$ [8].



Acetylides also react with electrophilic acetylenes and diazomethane to yield products in which carbon-carbon bonds have formed [9]. Diazomethane, which is known to be a carbene precursor, reacts with $(\mu\text{-pph}_2)\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}\equiv\text{C}^i\text{Pr})$ to give $(\mu\text{-H})(\mu\text{-pph}_2)\text{Ru}_3(\text{CO})_7(\mu_3\text{-}\eta^4\text{-CH}_2=\text{C}-\text{CC}^i\text{Pr}=\text{CH})$ via the allenyl complex $(\mu\text{-pph}_2)\text{Ru}_3(\text{CO})_8(\mu_3\text{-}\eta^3\text{-CH}_2=\text{C}=\text{C}^i\text{Pr})$ [10].



Acid induced isomerization of $(\mu\text{-H})\text{M}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}\equiv\text{CCPh}_2\text{OH})$, ($\text{M}=\text{Ru,Os}$), involves hydroxide transfer from carbon to metal atoms [11]. This reaction may be regarded as an intramolecular oxidative addition



of an alcohol with carbon-oxygen bond cleavage. Hydrogenation of $(\mu\text{-pph}_2)\text{Ru}_3(\text{CO})_8(\mu_3\text{-}\eta^2\text{-C}\equiv\text{CBu}^t)$ gives $\text{CH}_2=\text{CHBu}^t$ and the coordinatively unsaturated cluster $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu\text{-pph}_2)$ [12].

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