Synthesis and Reactivity of Cluster Bound Acetylides

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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 (RC≡C-) have recently provided some interesting chemistry. The acetylide, which is related to C=O and C≡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 acetylide 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$_3$NO in most cases and photochemically in a few cases. Thermal reaction of Ru$_3$(CO)$_{12}$ with HC≡CBut produces ($\mu$-H)Ru$_3$(CO)$_9$(μ-$\eta^2$-C≡CBut) [3]. Dirhenium decacarbonyl Re$_2$(CO)$_{10}$ reacts photochemically with HC≡CPh to yield ($\mu$-H)Re$_2$(CO)$_8$(μ-$\eta^2$-C≡CPh) [4].

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\text{Ru}_3(\text{CO})_{12} + \text{HC≡CBut} \xrightarrow{\Delta} \quad \text{CO} + 3\text{CO}
\]

\[
\text{Re}_2(\text{CO})_{10} + \text{HC≡CPh} \xrightarrow{\text{hv}} \quad \text{CO} + 2\text{CO}
\]

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

The \( \mu_3-\eta^2 \) acetylides \((\mu\text{-pph}_2)\text{Os}_3(\text{CO})_9(\mu_3-\eta^2-\text{C}≡\text{CPh})\) and \((\mu-\text{H})\text{Ru}_3(\text{CO})_9-(\mu_3-\eta^2-\text{C}≡\text{CPh})\) also react with nucleophiles [6]. The regiospecificity 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 \((\mu-\text{H})\text{Ru}_3(\text{CO})_9-(\mu_3-\eta^2-\text{C}≡\text{CPh})\), reactions with phosphites and phosphines yield only substitution products of the type \((\mu-\text{H})\text{Ru}_3(\text{CO})_8(\mu_3-\eta^2-\text{C}≡\text{CPh})(\text{L})\) [7]. Carbonyl substitution occurs regiospecifically on the ruthenium atom \( \sigma \) bonded to the acetylide. The metallic nucleophile such as \([\text{NiCp(CO)}]_2\) reacts with \((\mu-\text{H})\text{Ru}_3(\text{CO})_9(\mu_3-\eta^2-\text{C}≡\text{CPh})\) to yield a mixed metal vinyldene cluster \((\mu-\text{H})(\eta^5-\text{C}_5\text{H}_5\text{Ni})\text{Ru}_3(\text{CO})_9(\mu_4-\eta^2-\text{C}≡\text{CHPh})\) [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 \((\mu\text{-pph}_2)\text{Ru}_3(\text{CO})_9(\mu_3-\eta^2-\text{C}≡\text{CPh})\) to give \((\mu-\text{H})(\mu\text{-pph}_2)\text{Ru}_3(\text{CO})_7(\mu_3-\eta^2\text{CH}_2\text{C}≡\text{CPh})\text{=CH})\) via the allenyl complex \((\mu\text{-pph}_2)\text{Ru}_3(\text{CO})_8(\mu_3-\eta^3\text{CH}_2\text{C}≡\text{CPh})\) [10].
Acid induced isomerization of \((\mu-H)M_3(CO)_9(\mu_3-\eta^2-C\equiv C\text{C}p_2\text{OH})\), (M=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 \((\mu-\text{pph}_2)\text{Ru}_3(CO)_3(\mu_3-\eta^2-C\equiv \text{Bu})\) gives \(\text{CH}_2=\text{CHBu}^+\) and the coordinatively unsaturated cluster \((\mu-H)\text{Ru}_3(CO)_9(\mu-\text{pph}_2)\) [12].

References


