

Transition Metal Ketenes

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The mechanism of Fischer-Tropsch catalysis is presently believed to proceed via reactions involving methylene species on metal surfaces [1]. Muetterties, Herrmann, and Katzer [2] have suggested that carbonyl carbene coupling to form an intermediate ketene complex is one reaction path which could lead to oxygen-containing products. Support for these ketene intermediates arises from the ever increasing number of isolable, transition metal ketene complexes and their subsequent reactivity.

Transition metal ketenes have been observed in several different bonding arrangements. C,O and C,C π -bonding to one or two metal centers have been reported. Terminal, MRC=C=O, and μ_3 cluster bridged ketene complexes are also known. There are three primary methods for synthesizing transition metal ketenes. Substitution reactions bind a ketene to the metal center by displacement of a weakly bound ligand [3]. Dehydrohalogenation, a general synthetic route to ketene complexes of Zr and Ti, involves proton abstraction from the acyl-halo complex followed by displacement of the halogen by the ketene oxygen [4]. Insertion of a carbonyl into the metal carbon bond of a methylene ligand is, however, the most common method for preparing metal ketenes [5]. CO insertion into other alkylidenes and alkylidyne complexes has been observed as well, Fig. 1. Labeling and reactivity studies on several systems

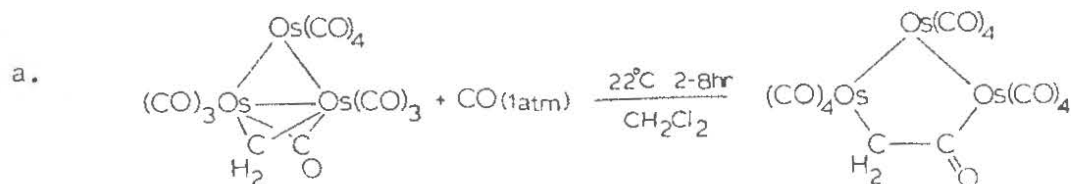
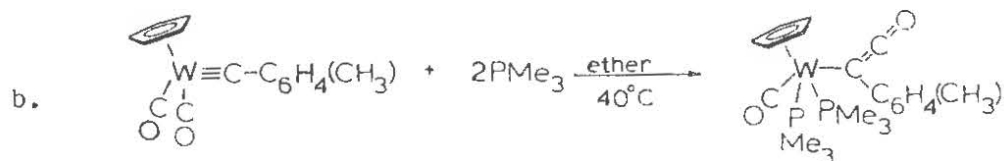
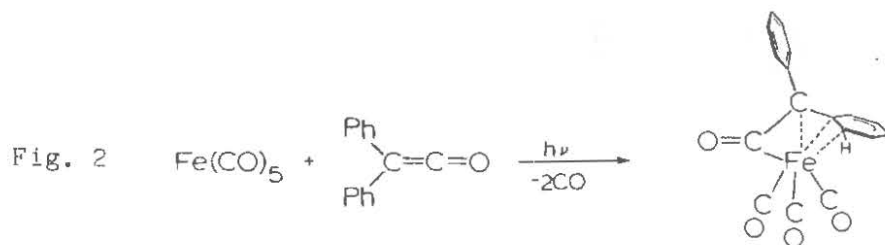


Fig. 1



indicate that both internal carbene-carbonyl coupling [5b,c,6] and insertion of external carbon monoxide [7] are possible pathways for the formation of metal ketenes.

Herrmann has demonstrated that reversible cleavage of the carbon-carbon bond of ketene complexes can occur [8]. Iron pentacarbonyl and diphenylketene were allowed to react in a ^{13}C enriched CO atmosphere, the resulting σ -acyl, π -allyl complex showed ^{13}C label incorporation into the metal ketene carbonyl site, Fig. 2. Since labeled carbon monoxide was not incorporated into the free ketene under reaction conditions, these results indicated that



the carbon-carbon bond of the ketene must be reversibly cleaved. When Deeming and Arce [9] reacted ketene with $\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$, they obtained $\text{Os}_3(\text{CO})_{10}(\mu\text{-CO})(\mu\text{-CH}_2)$ which upon heating converted to the ketenylidene species $\text{H}_2\text{Os}_3(\text{CO})_9(\mu_3\text{-CCO})$ previously reported by Shapley and coworkers [10]. These cases clearly demonstrate that internal carbene-carbonyl coupling (which results in metal bound ketene complexes) can be a readily reversible process.

Deoxygenation and decarbonylation are common decomposition pathways exhibited by ketene complexes of transition metals [11]. The trinuclear clusters $\text{H}_2\text{M}_3(\text{CO})_9(\text{CCO})$ $\text{M}=\text{Os}, \text{Ru}$ react with H_2O or MeOH to give the corresponding μ_3 -acid or μ_3 -ester [10,12]. Similarly, Geoffroy has shown that reaction of H_2O or MeOH with the bridging ketene $\text{Os}_3(\text{CO})_{12}(\eta^2(\text{C},\text{C})\mu\text{-CH}_2\text{CO})$, Fig. 1a, produces acetic acid or methyl acetate and $\text{Os}_3(\text{CO})_{12}$ [5c]. Hydrogenation of several ketene systems produces oxygenated hydrocarbons [5c,13]. This reactivity demonstrates that Fischer-Tropsch products can be produced from transition metal bound ketenes, suggesting their involvement in catalytic CO hydrogenation.

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