Applications of Flash Vacuum Pyrolysis and Related Studies on Alkyne Trimetallic Clusters

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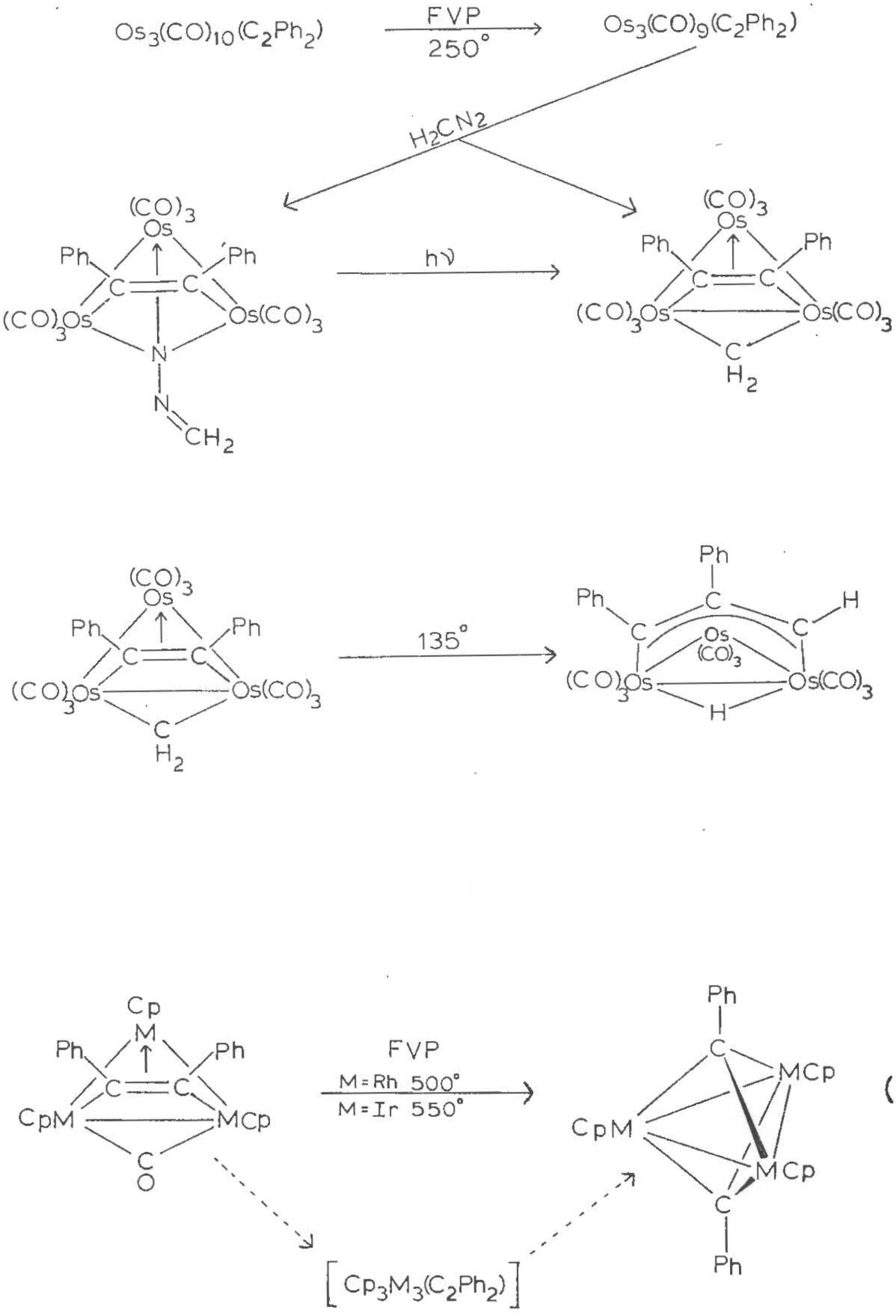
The study of organometal cluster compounds in recent years has provided a wealth of new information concerning the possible bonding modes and reaction pathways for hydrocarbons interacting with multimetal centers. Coordinatively unsaturated clusters and "lightly stabilized" derivatives have played an important role in the development of this chemistry.[1] Unlike the majority of coordinatively saturated clusters, these compounds are highly reactive at room temperature and below facilitating the characterization of thermally unstable intermediates. Unfortunately, very few highly reactive metal cluster compounds of this sort have been synthesized and the further development of mechanistic organometal cluster chemistry is limited by the small number available.

As a new approach to this problem we have employed the technique of flash vacuum pyrolysis (FVP) to generate reactive organometallic clusters and to induce novel structural rearrangements. This technique, which has been used by organic chemists for more than 15 years, is characterized by high vacuum distillation of the reactant through a heated tube where contact times are short ($10^{-3}$to 10^{-1}sec) followed by rapid condensation of the products at low temperature.[2]

Flash vacuum pyrolysis of $Os_3(CO)_{10}(C_2Ph_2)$ at 250°C results in efficient decarbonylation to yield coordinatively unsaturated $Os_3(CO)_9$-(C_2Ph_2).[3] The ability to cleanly generate this highly reactive compound has allowed its isolation and complete characterization as well as a systematic investigation of its reactivity. One of the most remarkable reactions is that of $Os_3(CO)_9(C_2Ph_2)$ with diazomethane.[4] This reaction proceeds rapidly at room temperature to yield nearly equal amounts of a thermally stable μ-diazomethane adduct and a μ-methylene complex. Photolysis of the diazomethane complex converts it into the methylene derivative by intramolecular loss of dinitrogen. Furthermore, heating a solution of the methylene complex results in coupling of the methylene and diphenylacetylene ligands to yield a new cluster containing a face bonded dimetalloallyl ligand. (Scheme)

Related studies have been carried out on the compounds $Cp_3M_3(CO)$-$C_2Ph_2)$ (M = Rh, Ir).[5] Although these are isoelectronic with Os_3-$(CO)_{10}(C_2Ph_2)$ they exhibit a pronounced difference in behavior when subjected to FVP. The rhodium and iridium compounds were unreactive at the temperature used to decarbonylate $Os_3(CO)_{10}(C_2Ph_2)$ (250°C). At higher temperatures (500-600°C) decarbonylation occurs; however, it is accompanied by alkyne cleavage to yield stable bisalkylidyne clusters.[6] (equation 1) Additional experiments established that the alkyne cleavage occurs intramolecularly on the trimetallic framework. Although alkyne cleavage has previously been shown to occur at metal surfaces to yield surface carbyne fragments,[7] it has not been established how many metal centers are required to facilitate cleavage of the carbon-carbon triple bond. This organometallic model system establishes the viability of a trimetal center as a template for the decoupling of an alkyne.

Scheme:


Os3(CO)10(C2Ph2)
FVP
250°
Os3(CO)9(C2Ph2)
H2CN2
hν
135°
FVP
M=Rh 500°
M=Ir 550°
[Cp3M3(C2Ph2)]
(CO)3
Os
Ph
C
N
CH2
H2
H
CpM
MCp
Cp
M
O

(1)

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6. Trimetallic bisalkylidyne clusters of cobalt and rhodium have been synthesized previously from the reaction of mononuclear cyclopentadienyl complexes of these metals with alkynes in solution at elevated temperatures. No information is available concerning the mechanism of these reactions.
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