Thermal and Photochemical Reactivity of
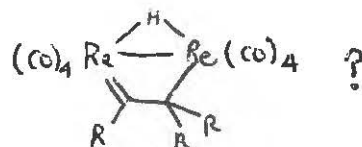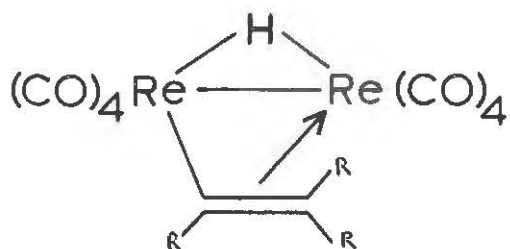Dirhenium Hydrido-Alkenyl Carbonyl Compounds

Philip O. Nubel   Final Seminar   August 11, 1983

The photochemistry of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ has been studied extensively within the past several years, particularly with respect to substitution by phosphorus [1] and, to a lesser extent, nitrogen [2] ligands. Substitution has also been effected by thermal means [3] and through the use of R_3NO [4]. Reactions of these compounds with unsaturated hydrocarbons (e.g., olefins and acetylenes) have received much less attention despite potential relevance to catalytic processes such as isomerization, hydrogenation, oligomerization, etc.

UV photolysis of $Re_2(CO)_{10}$ at 25° in the presence of ethylene, terminal olefins, or 2-butene results in formation of μ-hydrido, μ-alkenyl dirhenium octacarbonyl complexes in high yield [5]. The bridging alkenyl ligand forms a σ bond to one Re atom and a π bond to the other.

Analogs to the dirhenium hydrido-alkenyl compounds exist in osmium cluster chemistry; reactions of simple olefins with tri- and tetra-osmium carbonyl compounds yield μ_2-hydrido, μ_2-alkenyl tri- [6] and tetraosmium [7] products, respectively. In solution, the μ-alkenyl ligand of the dirhenium and triosmium complexes undergoes a rapid fluxional process at room temperature in which the σ and π bonds of the alkenyl group are interchanged between the bridged metal atoms [8].

The dirhenium hydrido-alkenyl compounds react with a variety of substrates under mild thermal conditions. Treatment with pyridine, $P(OMe)_3$, PMe_3, or $P(OPh)_3$ at 25° results in elimination of olefin and formation of 1,2-eq,eq-$Re_2(CO)_8L_2$. Kinetics investigations of reactions with pyridine are consistent with a mechanism which begins with intramolecular C-H reductive elimination. Treatment with bis(diphenylphosphino)methane (dppm) affords a dppm-bridged complex, $Re_2(CO)_8(dppm)$; reaction with PPh_3 or $P(n-Bu)_3$ initially generates 1,2-ax,eq-$Re_2(CO)_8L_2$ which thermally isomerizes to 1,2-ax,ax-$Re_2(CO)_8L_2$. The hydrido-alkenyl compounds react with ethylene, terminal olefins, or cis- (but not trans-) 2-butene to afford the hydride- and alkenyl-exchanged hydrido-alkenyl species. Treatment with phenylacetylene yields a μ-hydrido, μ-acetylido dirhenium octacarbonyl complex. Reaction with H_2 generates $H_2Re_2(CO)_8$.

Photolysis of $(\mu\text{-H})(\mu\text{-CH=CH}_2)\text{Re}_2(\text{CO})_8$ in the presence of ethyle
affords μ-hydrido, μ-butenyl dirhenium octacarbonyl complexes. A
mechanism is proposed in which the initial step is photo dissociatic
of CO, inasmuch as photolysis in the presence of ^{13}CO or PPh_3 result
in CO substitution. Subsequent steps in the formation of the hydric
butenyl species are coordination of ethylene, insertion of ethylene
in the Re-H or Re-ethenyl σ bond, re-coordination of CO, C-C or C-H
reductive elimination to yield $\text{Re}_2(\text{CO})_8$(1-butene), and oxidative
addition of a vinylic C-H bond of coordinated butene. Slow catalyti
production of 1-butene and trans-3-hexene occurs in the photochemica
reaction of the hydrido-ethenyl complex with ethylene; butene format
is the result of thermal reaction of the hydrido-butenyl dirhenium
species with ethylene, while hexene results from photochemical react
Removal of photo dissociated CO from the system via an ethylene-purg
during photolysis results in subsequent catalytic production of bute
and hexene under thermal (25°) conditions. Photolysis of $(\mu\text{-H})$-
$(\mu\text{-CH=CHCH}_3)\text{Re}_2(\text{CO})_8$ in the presence of propylene yields 2-hexene.
A general mechanism for dimerization of olefins is proposed in which
a dinuclear metal catalyst effects the insertion of one olefin into
a vinylic C-H bond of another. Additionally, cis→trans and trans→ci
isomerization of the bridging alkenyl ligand of $(\mu\text{-H})(\mu\text{-CH=CHR})\text{Re}_2(\text{C}$
complexes is effected photochemically.

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