NOTES

## Possible Role of Hydrido–Metal Complexes in Metathesis, Isomerization, Dimerization, and Polymerization of Alkenes

Much evidence (*1–5*) has been obtained in the last few years that olefin metathesis and ring-opening polymerization of cyclo-alkenes are chain reactions, with carbenes as the chain carriers reversibly reacting with complexed alkenes to generate new carbenes and alkenes via intermediate metallocyclobutanes.
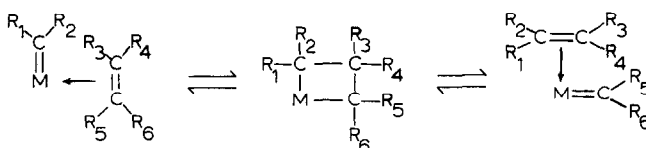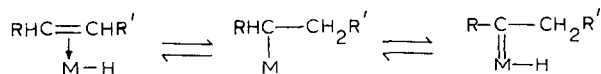

For those homogeneous systems where the co-catalyst is a main group alkyl compound, some of the alkyls are believed to transfer to the transition metal ions which convert them to the initial carbenes (*2, 6*). However, the problem of initiation has been raised (*2*) for homogeneous systems without an alkyl activating agent; this problem is particularly pertinent to heterogeneous catalysts such as those prepared from carbonyls and oxides of Mo, W, Re on alumina or silica.

Recently we obtained good evidence (*7*) that metal hydrides are responsible for ring-opening polymerization and dimerization reactions of norbornene catalyzed by several transition metal halides; an alkyl-activating agent is not required. Since then we have observed that the activities in chloroform solution of some cycloocta-1,5-diene (COD) complexes of Ir, Ru, and Os halides for this polymerization are directly
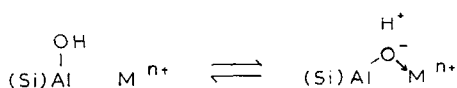
related to the concentrations of hydride ligands estimated from solid-state ir bands in the range 1900–2100 cm^{-1}. The complexes were prepared by heating aqueous ethanolic solutions of the hydrated trihalides with COD (COD/metal = 2/1) at 50°C for several days. The presence of hydride was confirmed by Fourier transform NMR spectroscopy (Ir, -10.7 ppm; Os, -1.8 ppm, values relative to TMS). Using this technique we have also detected hydrido–tungsten complexes (-26.1 ppm, value relative to TMS) in the well-known metathesis catalyst, $WCl_6/EtOH/EtAlCl_2$ in benzene solution, at both 1/1 and 6/1 Al/W ratio. We conclude (*7*) that the role of hydride is to isomerize olefin reversibly to carbene complexes via metal alkyl formation, thereby providing a likely means of carbene initiation and chain termination. Metathesis is therefore directly linked to other reactions, such as isomerization,

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dimerization, and polymerization, where

$$RHC{=}CHR' \underset{M{-}H}{\downarrow} \rightleftharpoons RHC{-}CH_2R' \mid M \rightleftharpoons R{-}C{-}CH_2R' \underset{M{-}H}{\parallel}$$

alkyl species are also key intermediates, and indeed is often accompanied by one or more of these reactions (8). When corresponding heterogeneous catalysts consisting of transition metal ions on hydroxylic supports are considered, it is logical that the same mechanisms apply since individual metal ions often retain their distinctive catalytic properties irrespective of phase. This leads to the suggestion that metal hydrides are also formed in such systems as $Mo(CO)_6$ on alumina (9), Cr oxide (10), and Mo, W, and Re oxides (11) on silica and alumina, Ni oxide on silica (12), group VIII ions in Y-zeolites (13), and in many others. Metal hydrides derived by reaction of Ti and Zr alkyls or allyls with hydroxyl groups on silica are now known to polymerize ethylene (14, 15). However, the much more general formation and role of hydrides that we envisage (e.g., even in MoO_3/Al_2O_3 activated for metathesis) has not hitherto been discussed.

It is usually accepted that, when a transition metal ion is coordinatively unsaturated in the surface of a hydroxylic oxide, the following interaction may take place generating Brønsted acidity. We now propose

$$\begin{array}{cc} OH \\ \mid \\ (Si)Al \quad M^{n+} \end{array} \rightleftharpoons \begin{array}{c} H^+ \\ O^- \\ (Si)Al \quad M^{n+} \end{array}$$

that if the ion is in a low or perhaps intermediate oxidation state, the alternative of oxidative addition yielding a surface metal hydride may be possible. A donor ligand such as an alkene already on the metal may

$$(Si)Al{-}O{-}M^{(n+2)+} \mid H$$
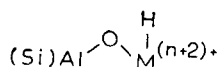
be necessary for this reaction, and because of the ensuing insertion reaction the hydride may only have a very transient existence. Alternatively alkene may first add a proton yielding a carbonium ion which then directly forms a metal–alkyl intermediate. Obviously if oxidative addition to a hydroxy group $(H^+ O^- -)$ occurs, it should also be possible with an alkoxy species $(R^+ O^- -)$. The formation of many metal hydrides in protic solvents is described in just this fashion (16), and the following facts may be cited as evidence that such a reaction also occurs in heterogeneous systems. Thus, hydrogen is evolved when $Mo(CO)_6$ reacts on Al_2O_3 (17), indicating the intermediacy of a molybdenum hydride complex. Hydroxylic, acidic, organic materials such as resorcinol (18) or partially oxidized charcoal (19) also react with $Mo(CO)_6$ giving highly active metathesis catalysts, whereas nonoxidized charcoal is inert in this respect (19). Again, it has often been noted that the presence of acidic hydroxyl groups on inorganic supports in the vicinity of the metal ion (12, 13) enhances activities for ethylene dimerization, and very recently the marked promotional effect of HCl gas for this reaction using catalysts prepared by depositing $RhCl_3$ on SiO_2 has been reported (20). A relevant homogeneous example of the vital role of oxidative addition of protonic acids is that the most active iridium metathesis catalyst is obtained by adding CF_3CO_2H to trifluoroacetatobis(cyclooctene)iridium (21), which by itself is inert. Perhaps a corresponding heterogeneous analogy is the observation that treatment of WO_3/SiO_2

with HCl gas increases its activity for 1-butene disproportionation (*22*).

There is also a common mechanistic theme based on a four-centered complex including the metal ion for all these reactions.

Metathesis: Reversible addition of an alkene to a carbene-metal bond (Eq. 1).

Isomerization: Reversible insertion of an alkene into a hydride-metal bond.
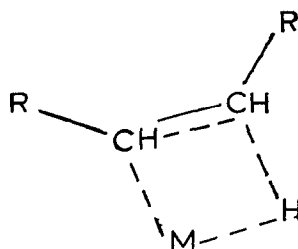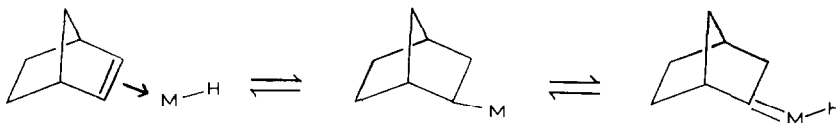

Dimerization and polymerization: Alkene insertion into an alkyl-metal bond.
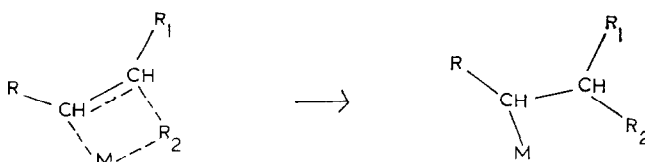
Considering reactions of ethylene, metal ions on the left-hand side of the transition series with no or very few *d*-electrons form weak olefin complexes such that polymerization, i.e., extension of the alkyl chain, is preferred to alkyl reversal to olefin and metal hydride (*14*). However, the ions in Group VIII, with filled d^π-orbitals and thus potentially important back-bonding to p^π-orbitals of the olefin, form stronger π-complexes with the result that dimerization is dominant. There are also interesting vertical trends. Thus, activated CrO_3/SiO_2 (*10*) is a well-known polymerization catalyst but, on descending

Group VI, oligomerization and dimerization become more pronounced. A corresponding vertical trend towards easier formation of carbenes and thereby catalysis of metathesis is also noted (*8*). Obviously *d*-orbital population and ligand field splitting are quite critical in optimizing formation of carbenes in competition with olefin complexes. This competition is biased in favor of the former with strained cycloalkenes, thus facilitating ring-opening polymerization (*7*), because isomerization shifts the double bond to the relatively more stable exocyclic position. It is not surprising that

the metals which are active for such polymerizations are more numerous than those for the metathesis of simple alkenes.

Another major advantage of the hydride theory is the possibility of repetitive initiation and termination on one metal site.

Even if alkyl from an activating agent is present and is the immediate source of the first carbene, hydride must again take over if there is multiple chain termination and renewal. A less obvious but possible role of such an alkyl, e.g., ethyl, is addition to

reactant olefin giving a new secondary alkyl, $R-\dot{C}H-CH(C_2H_5)-R_1$, which should convert more easily to the corresponding carbene. An analogous phenyl addition to olefin may be the answer to the mode of initiation of metathesis in the homogeneous $C_6H_5WCl_3$ catalyst (2).

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