Mechanism of Initiation of Ring-opening Polymerization of Norbornene Catalysed by Transition-metal Halides

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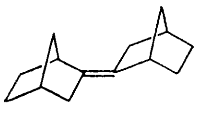
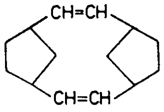
Summary Low molecular-weight products have been obtained during ring-opening polymerization of norbornene catalysed by several transition-metal halides; their identities and other evidence show that hydrido-metal complexes are involved in both dimerization reactions and carbene initiation.

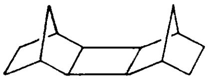
There is now good evidence[1–4] that a mechanism involving metal–carbene complexes as chain-carriers operates for both olefin metathesis and ring-opening polymerization of cycloalkenes. We have therefore analysed systems consisting of norbornene (NBE) with several catalysts[5] and solvents, seeking low molecular-weight products whose identities might help to elucidate the mechanism of carbene initiation, and now report our major findings.

Polymerization occurred readily at ambient temperatures using WCl_6, $ReCl_5$, and $MoCl_5$ in dry carbon disulphide or benzene but only the first two halides caused significant formation of the four isomeric dimers (I). The identities of (I) were confirmed by synthesis from norbornan-2-one using the McMurry and Fleming[6] procedure for reductive dimerization of ketones. Smaller amounts of trimers, homologous to (I), were also isolated. The dimers (II), and (III), which might have been expected from concerted and non-concerted mechanisms involving pair-wise exchange of alkenes and carbenes,[2,3] were never detected. Furthermore, WCl_6 under identical conditions was unable to rupture the C_4-rings in the three *trans*-[2 + 2] dimers, (III). Norbornylbenzene was also obtained using benzene solvent and detailed kinetic analyses showed that while alkylation was independent of polymerization, a common intermediate was indicated for the latter reaction and dimerization. Polymerization using WCl_6 was always accompanied by formation of 2-chloro- and 2,3-dichloronorbornane. Addition of trace amounts of water enhanced polymerization activity by an order of magnitude but increasing quantities eventually caused total inhibition. Polymerization was also significantly retarded but never completely suppressed by addition in benzene of excess butyl-lithium (WCl_6 treated with LiC_4H_9 is a weak metathesis catalyst).[7] As well as dimers a secondary alcohol, (IV), $C_{14}H_{22}O$, (Scheme) was also detected in the reactive water-WCl_6 systems. In contrast to the above catalysts the hydrates of the trichlorides of Ru, Os and Ir gave this alcohol as the most important, and often exclusive, C_{14} product, and 2-hydroxynorbornane was also isolated. These catalysts were virtually inactive in alkylating benzene with NBE. Polymerization of bicyclo[2.2.2]octene was just detectable using WCl_6, while cyclohexa-1,3-diene, but not its hepta- and octa-homologues reacted in similar fashion showing that easy ring-opening is not peculiar to bridgehead olefins but is rather a function of strain energy in these cyclic monomers.

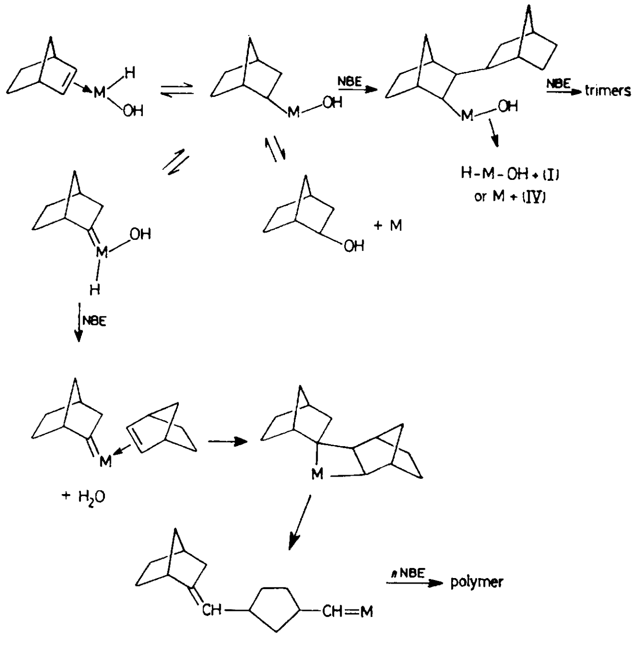

(I)



(II)


(III)

The results concur with the metallocyclobutane theory[1–4] (Scheme) but are against the view[3] that metallocyclopentanes may be the source of carbenes when metathesis catalysts do not contain a main group alkyl compound as an activating agent. While Brönsted acidity is clearly involved in alkylating benzene, separate metal-hydride complexes, increased in number for WCl_6 by a little water and diminished by LiC_4H_9, seem to be largely responsible for dimerization and essential for polymerization. Indeed we have found that a hydrated cyclo-octa-1,5-diene complex of $IrCl_3$,[8] which is very active in polymerizing NBE, has a strong solid-state i.r. band at 2060 cm^{-1} due to an Ir–H bond.[9] Thus in the case of WCl_6 such hydridic sites could arise from reaction of HCl and/or H_2O with W^{IV} subsequent to reduction of some W^{VI} by NBE. These sites then catalyse dimerization and/or polymerization as shown (Scheme). In view of the probable strong donation of charge, $p^{\pi} \rightarrow d^{\pi}$, in the carbene-metal bond the electron affinity of the metal ion, and thus the acidity of the hydride, could well be important in determining the relative significance of different reaction pathways.



SCHEME

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