## Mechanism of Initiation of the Metathesis of Norbornene using $W(CO)_3Cl_2(AsPh_3)_2$ as Catalyst

## Lajos Bencze,\* Anna Kraut-Vass, and László Prókai

Institute of Hydrocarbon and Coal Processing, Veszprém University of Chemical Engineering, Veszprém, P.O.B. 158, H-8201 Hungary

Low molecular-weight derivatives obtained during ring-opening polymerisation of norbornene using  $W(CO)_3Cl_2(AsPh_3)_2$  as catalyst indicate that a 2,3-hydrogen shift is a key step for the formation of the carbene initiator.

Catalyst systems having neither a preformed metallacarbene nor an alkyl group in any component represent a relatively minor class of metathesis initiators. While some recent investigations<sup>1,2</sup> point to a hydrogen transfer process in



W-complexes with alkenes, pathways for carbene formation are in most cases unresolved.

We reported recently that the ring-opening polymerization of norbornene (10 mmol) occurs readily in benzene solution (50 ml) at 80 °C using W(CO)<sub>3</sub>Cl<sub>2</sub>(AsPh<sub>3</sub>)<sub>2</sub> (0.05 mmol) as catalyst.<sup>3</sup> In order to elucidate the mechanism of carbene initiation the reaction was quenched by EtOH and the low molecular-weight products were identified by g.c.-mass spectrometry and comparison with authentic samples. The major product was ethyl norbornane-2-carboxylate (1) (m/z168(2.8%;  $M^+$ ), 139(11), 123(13), 101(100), 95(86), 73(24), 67(30), 66(14), and 41(12). Smaller amounts of di-(2norbornyl)ketone (2) ( $M^+$ , m/z 218, 5%) and the 2-ethoxycarbonyl derivative (3) ( $M^+$ , m/z 290, 0.7%) were also found besides some 2-chloronorbornane. Using methanol as a quenching agent the corresponding methyl derivatives of (1) and (3) were identified.

When water was added to the system  $(H_2O/W = 11)$  prior to the polymerization and the reaction quenched with a large quantity of cold water the polymer yield dropped from 65 to 10%. An increased quantity of (2) and 2-chloronorbornane was found in the benzene solution while the esters were missing. The acid (4)  $(M^+, m/z \ 140, 11.3\%)$  was identified in the aqueous phase.

The mechanisms of formation of (1)-(3) and (4) are



intimately connected: they appear to be products of addition of water or alcohols to the ketene (5) and its dimer (6) by analogy with the reactions of ketoketenes reported by Anet<sup>4</sup> and Hasek *et al.*<sup>5</sup>

This idea is further strengthened by the observation that when the system is partially poisoned by addition of  $D_2O$  prior to the polymerization and then quenched by EtOD the ester (1) formed is exclusively monodeuteriated, and the deuterium is situated in position 2. The ketone (2) contains two D atoms, each on the  $\alpha$  carbon atoms, *i.e.* in position 2 of the norbornane skeleton. These results show that the corresponding C-8 ketene is formed without any H–D scrambling, which occurs only in the hydrolysis or alcoholysis step (Scheme 1).

The reversible generic relationship between carbenes and ketenes *via* CO-carbene coupling and decoupling is well known in organic chemistry<sup>6,7</sup> and has recently been recognized in organometallic chemistry<sup>8-11</sup> also. It is readily envisaged now that the structure of the initial carbene ligand may be identified with a co-ordinated 2-norbornylidene species, and the ketene is formed by coupling with a neighbouring carbonyl ligand.

It is therefore to be expected that the activity of the catalytic system will be rather sensitive to carbene-trapping reagents, such as organic carbonyl compounds.<sup>12</sup> Thus, when benzaldehyde was added to the norbornene– $W(CO)_3Cl_2(AsPh_3)_2$ benzene system prior to thermal activation, the ring-opening polymerisation was inhibited and the benzylidene-norbornane J. CHEM. SOC., CHEM. COMMUN., 1985

This further supports the assumption that the hydrocarbon part of the initiating metallacarbone complex may be identified with a 2-norbornylidene group formed by a 2,3-(1,2-) hydrogen shift in the co-ordinated alkene.

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