Homogeneity of Olefin Metathesis Reactions Catalysed by Co-ordination Complexes

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Summary A soluble WCl_6-based olefin metathesis catalyst is described.

IT has been recently suggested[1] that olefin metathesis reactions catalysed by co-ordination complexes, and particularly those derived from WCl_6, are in fact heterogeneous in nature and that the primary catalytic activity for metathesis resides in the insoluble fraction of the catalyst. We present here an example of a typical WCl_6-based co-ordination complex catalyst that has been prepared and used for olefin metathesis, where the total metathetic activity has been found to reside in the soluble fraction of the catalyst, while no metathetic activity was observed with the insoluble part. This finding stands well in accord with the current view concerning homogeneous catalysis in olefin metathesis but clearly disagrees with the suggestion in ref. 1.

Four parallel experiments† on the metathetical cyclo-oligomerization of cyclododecene into cyclopolyolefins[2] using a WCl_6–$EtAlCl_2$ co-ordination complex catalyst gave the following results. Experiment 1 was conducted under the conventional *in situ* formation of the catalyst in the presence of olefin, where a clear solution of WCl_6 followed by a clear solution of $EtAlCl_2$ were added to a stirred olefin solution. A flocculent precipitate was formed immediately. In experiment 2 a preformed catalyst suspension was obtained from WCl_6 and $EtAlCl_2$ by addition of a clear solution of $EtAlCl_2$ to an agitated clear solution of WCl_6. A flocculent precipitate was formed immediately. The whole suspension (containing both soluble and insoluble portions) was added to the olefin solution. For experiments 3 and 4 a preformed catalyst suspension as above was divided by filtration into a soluble portion and an insoluble residue. In experiment 3 the clear solution filtrate of the preformed catalyst was added to the olefin solution while in experiment 4 the residual insoluble solids were added as a suspension to the olefin solution. Experiments 1, 2, and 3 yielded similar distributions of cyclo-oligomers with relatively high conversion obtained through metathesis,[2] while in experiment 4 no metathetical cyclo-oligomerization took place.

Another example illustrating the homogeneity of a WCl_6-based metathesis catalyst is provided by an experiment conducted, but incorrectly interpreted, by Muetterties and Busch.[1] These authors stated that in the most active alcohol-modified WCl_6–$2EtAlCl_2$ system, solids were visible (laser beam light) only after 5—10 min, whereas metathesis equilibrium required only 2—3 min.

We believe that in order to justify the generalization claimed in ref. 1, more concrete evidence is needed than was presented.

(*Received, 30th December 1974; Com. 1573.*)

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† The same conditions were used in all four experiments concerning catalyst origin, solvent purity, inert atmosphere, concentrations proportions, reaction time, work-up procedure, analysis technique, *etc.*

[1] E. L. Muetterties and M. A. Busch, *J.C.S. Chem. Comm.*, 1974, 754.

[2] R. Wolovsky and Z. Nir, *Synthesis*, 1972, 134.