

Haines R J & Leigh G J. Olefin metathesis and its catalysis.

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The paper provided a summary and critical analysis of the chemical literature relating to alkene and alkyne metathesis. An initial description of the scope of the reaction was followed by a survey of the catalytic systems employed and a discussion on the nature of the catalytic site. The final section of the paper was devoted to an evaluation of the various mechanisms proposed for the reaction and to the authors' preferences in this connection based on the relevant and sometimes apparently unrelated information available. [The *SCF*® indicates that this paper has been cited in over 115 publications.]

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This review was written over a period of two years, between 1972 and 1974. In 1972 RJH joined the research group of J. Chatt at the University of Sussex as Visiting Fellow. At that time, Chatt and his colleagues were intrigued by the exciting advances in the study of metathesis reactions of alkenes and alkynes. It was known that symmetrical acetylenes ( $RC\equiv CR$  and  $R'C\equiv CR$ ) could react in the presence of an appropriate catalyst to produce a mixture containing a statistical amount of the mixed acetylene  $RC\equiv CR'$ , as if the units  $RC$  and  $R'C$  were combining randomly with each other. This raised the prospect of the synthesis of nitriles ( $RC\equiv N$ ) from dinitrogen and an acetylene, and we collaborated in the attempts to achieve this.

It soon became clear that the chances of success were slender, if only because the reac-

tion we wanted to realise would be accompanied by significant enthalpy changes. We learned quickly that most of the proposed mechanisms for metathesis (the terms dismutation and disproportionation were also in vogue at that time, but we favoured metathesis) were speculative. However, the literature contained pieces of apparently unrelated information that suggested that fission of carbon-carbon double (or triple) bonds really did occur and that monocarbon species ("carbenes" and "carbynes") really were involved. Electron-rich olefins clearly split to give carbenes.<sup>1</sup> Cyclopropane and methylcyclopropane had been produced by metathesis of ethylene.<sup>2</sup> Moreover, statistical analysis of the products of metathesis of acyclic and cyclic olefins suggested the presence of carbene intermediates.<sup>3</sup> However, none of the information had been collated, and we decided that a comprehensive review of alkene and alkyne metathesis was required that would summarise and evaluate critically the available information and speculate in an informed manner.

The gestation period was long. RJH returned to South Africa and was buried in an avalanche of university teaching. For two years the project stuttered along, but it matured and improved with time. When it finally appeared in 1975, the review was immediately seized upon as a useful and apposite contribution to the subject and a reliable source of references. Perhaps the fact that we were not wedded to any particular mechanistic interpretation (although the one that we favoured is probably correct) helped us to an unbiased presentation.

All this has its ironic side. We were not known to the practitioners in this particular field, and resentment was expressed in some quarters toward the publicity that accrued to our review. Furthermore, the system we chose for laboratory study proved to be an effective olefin metathesis catalyst<sup>4</sup> but under certain conditions could be explosive. Eventually we decided to leave the field to more valiant souls. We have, between us, published three experimental papers on alkene and alkyne metathesis.<sup>4-6</sup> None has achieved the resonance of this review.

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