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Preliminary communication

THE CATALYSIS OF ALKENE ISOMERISATION, OLIGOMERISATION, AND POLYMERISATION BY CATIONIC NITROSYLRHODIUM COMPLEXES

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Summary

The complex $[Rh(NO)(NCMe)_4][BF_4]_2$ catalyses the isomerisation of terminal to internal alkenes, the oligomerisation of branched alkenes such as 2-methylpropene, and the stereospecific polymerisation of buta-1,3-diene to *trans*-1,4-polybutadiene.

Catalysis by transition metal nitrosyl complexes, particularly of the olefin metathesis reaction [1], is becoming increasingly important [2]. We wish to report the results of a preliminary study which shows the versatility of $[Rh(NO)(NCMe)_4][BF_4]_2$ (I) [3] as a catalyst for alkene isomerisation, oligomerisation, and polymerisation, and the effect of nitrile substitution by phosphine ligands on its efficacy. It is interesting that the dicationic nitrile complex $[Pt(NCMe)_4][BF_4]$ has recently been found [4] to selectively dimerise branched olefins.

The dication I catalyses* the oligomerisation of branched alkenes. For example 2-methylpropene gives a mixture of dimers, trimers, and tetramers which have been separated by preparative GLC and characterised by ^1H NMR spectroscopy [Scheme 1 shows the sequence of formation, and the identity of the products; the most likely intermediates are η^3-allylhydridometal species. Unsubstituted alk-1-enes undergo only isomerisation, for example hex-1-ene is converted quantitatively to hex-2-ene, confirming the occurrence of the alkene isomerisation processes shown in Scheme 1.

The presence of *cis*-but-2-ene, which is itself not oligomerised, suppresses the trimerisation of 2-methylpropene and at higher relative concentrations of the former evidence for codimerisation is found. Such observations suggest alkene coordination to the η^3-allyl intermediate to be an essential step.

Buta-1,3-diene and cyclohexa-1,3-diene are rapidly polymerised in the presence of I giving white solids. IR studies show [6] the product from the former to be

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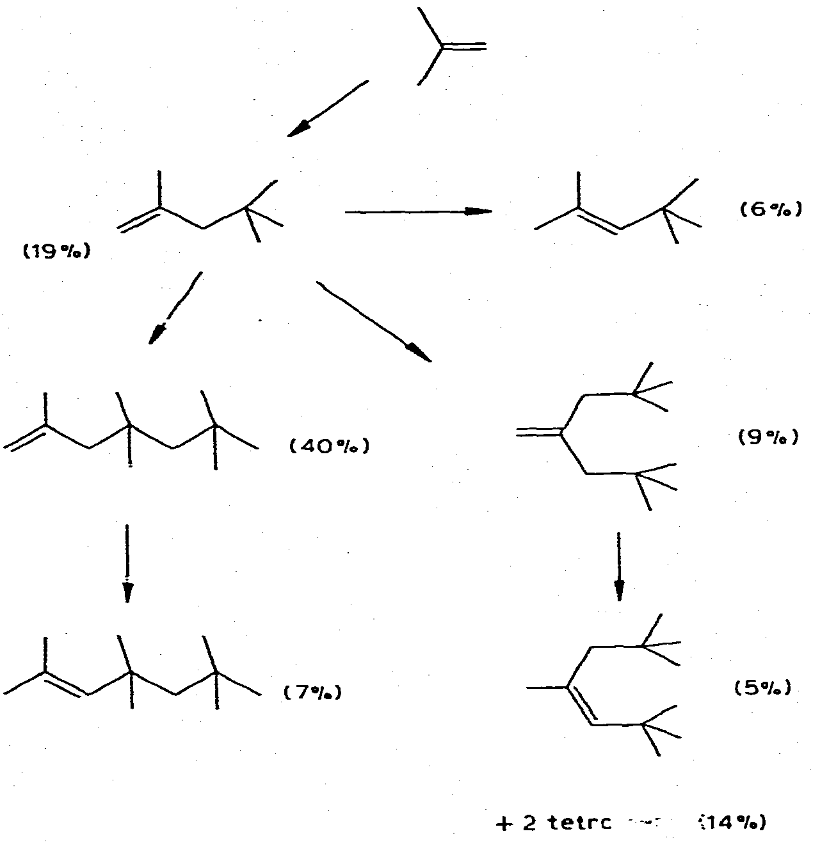
*The catalytic reactions are usually carried out in $MeNO_2$, at room temperature, for 16 h, using a 100/1 ratio of substrate to catalyst.



SCHEME 1

exclusively (not less than 95%) *trans*-1,4-polybutadiene. In contrast isoprene is oligomerised by I affording tetramers to decamers. The phosphine derivative, $[Rh(NO)(NCMe)_2(PPh_3)_2][BF_4]_2$ (II), however, under similar conditions to those used for the reactions of I, catalyses the formation of dipentene, and five trimeric products, from isoprene at 60°C. Under mild conditions II does not catalyse the oligomerisation of 2-methylpropene. Further studies of the catalytic behaviour of I and II and of their many derivatives [3] are in hand.

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