Catalytic Dimerisation of Olefins by a Cationic Platinum(II) Complex

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Summary The new complex $[Pt(MeCN)_4]$ $[(BF_4)_2]$ catalyses the dimerisation of branched olefinic monomers in nitromethane solution.

HOMOGENEOUS dimerisation of olefins promoted by compounds of transition metals other than Pt^{II} has been studied intensively.¹ Although a few systems have been investigated in detail,^{1,2} general knowledge of the mechanistic features of these catalytic processes is far from complete.

We report an investigation on the catalytic activity of Pt^{II} in the dimerisation of alkenes. We note that, beside the potential synthetic interest, Pt^{II} chemistry offers the unique opportunity of isolating stable alkene and alkyl complexes, species of the type believed to be involved in this process.

 $[Pt(MeCN)_4][(BF_4)_2]$ (I) was prepared by reaction of $[PtCl_2(MeCN)_2]$ with $AgBF_4$ (mol ratio 1:2) in anydrous acetonitrile. After evaporation and extraction with nitromethane, the product was crystallized from $MeNO_2$, giving colourless needles which are stable for weeks under dry conditions. Complex (I) was characterized by elemental analysis and ¹H n.m.r. spectroscopy.

the dimerisation of branched olefins, such as 2-methylpropene, 2-methylbut-2-ene, 2-ethylbut-1-ene, and cisand trans-4-methylpent-2-ene. In a typical experiment, when 2-methylbut-2-ene (20 cm³, 0.2 mol) was shaken for 3 h at room temperature with 15 cm^3 of a 0.02 M solution of (I) in MeNO₂, a 65% conversion of the monomer into a mixture of dimers occurred. No appreciable formation of higher oligomers was observed. The mixture was fractionated by preparative g.l.c. and the two main products (>95% of the mixture) were identified by ¹H and ¹³C n.m.r. spectroscopy³ as 2,3,4,4-tetramethylhex-l-ene (A) and 3,4,4,5-tetramethylhex-2-ene (B) in a molar ratio of 3.2:1. Analysis of the mixture at different times showed that compound (A) predominated at the beginning of the reaction. The ratio of (B): (A) increased with time, suggesting an isomerisation promoted by the catalyst. In fact, when pure (A) was shaken with a solution of the complex (I) in MeNO₂, isomerisation to (B) was observed.

We thank the Italian C.N.R. for financial support, and Mr. A. Saporito for experimental assistance.

At room temperature a solution of (I) in MeNO₂ induces

(Received, 20th October 1975; Com. 1179.)

¹ M. Herberhold, 'Metal *n*-Complexes,' Elsevier, New York, 1974, vol. II, part 2, pp. 226-233 and references therein.

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