

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

By AUGUSTO DE RENZI, ACHILLE PANUNZI,* and ALDO VITAGLIANO

(Istituto Chimico, Università di Napoli, 80134 Naples, Italy)

and GASTONE PAIARO

(Istituto di Chimica Analitica, Università di Padova, 35100 Padua, Italy)

Summary The new complex $[\text{Pt}(\text{MeCN})_4][(\text{BF}_4)_2]$ 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.

$[\text{Pt}(\text{MeCN})_4][(\text{BF}_4)_2]$ (I) was prepared by reaction of $[\text{PtCl}_2(\text{MeCN})_2]$ with AgBF_4 (mol ratio 1:2) in anhydrous 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.

At room temperature a solution of (I) in MeNO_2 induces

the dimerisation of branched olefins, such as 2-methylpropene, 2-methylbut-2-ene, 2-ethylbut-1-ene, and *cis*- and *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 cm³ of a 0.02M solution of (I) in MeNO_2 , 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 ^{13}C n.m.r. spectroscopy³ as 2,3,4,4-tetramethylhex-1-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 MeNO_2 , isomerisation to (B) was observed.

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

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

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

² R. Cramer, *J. Amer. Chem. Soc.*, 1965, **87**, 4717; L. S. Pu, A. Yamamoto, and S. Ikeda, *ibid.*, 1968, **90**, 7170.

³ F. C. Stehling and K. W. Bartz, *Analyt. Chem.*, 1966, **38**, 1467.