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Preliminary communication

THE CATALYTIC STEREOSPECIFIC DIMERISATION OF NORBORNADIENE TO 'BINOR-S'

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Summary

A wide variety of polynuclear cobalt carbonyl complexes bring about the title reaction but only in the presence of a Lewis acid cocatalyst.

It has long been known that some polynuclear metal carbonyls catalyse the stereospecific dimerisation of norbornadiene (NBD) to 'Binor-S' [1]. Schrauzer has proposed a π-complex multicentre mechanism for some of these reactions [1], but for catalysts such as $RCCo_3(CO)_9$ an alternative has been suggested [2]. We have studied this dimerisation in greater detail than hitherto and now give a preliminary account of our results.

We have found that many cobalt complexes act as catalysts. In approximate order of decreasing efficacy they are $Co_2(CO)_8 \sim (NBD)_2\ Co_2(CO)_4 > (Ph_2C_2)Co_2(CO)_4L_2 > RCCo_3(CO)_6L_3$ and $R = I > Br > Cl > H > Me > Ph$. Generally, increasing the degree of substitution of L = CO by L = t-BuNC or Ph_3P increases the catalyst efficacy. Other useful catalysts which have not yet been investigated in any detail are $Co_4(CO)_{12}$ and its substituted derivatives, and $[AgCo(CO)_4]_n$.

There is a marked solvent effect in these dimerisation reactions. Many will take place in, for example, benzene, but only at elevated temperatures. On the other hand, in dichloromethane they are rapid at ca. 30°C or below.

In most instances a Lewis acid cocatalyst is necessary. We have routinely used $BF_3 \cdot Et_2O$. In its absence, if dimerisation takes place it is slow and often not stereospecific (cf. ref. 3). In such cases e.g. with $ClCCo_3(CO)_9$ the presence of Lewis acid improves the catalyst performance.

Although light is not necessary, 'Binor-S' formation is often more rapid when the reaction mixtures are irradiated. This is especially so when the Lewis acid cocatalyst is absent. However, we have carried out the reactions in the dark.

Of special interest is the reaction involving $(Ph_2C_2)Co_2(CO)_6$ as a catalyst and

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$BF_3 \cdot Et_2O$ as a cocatalyst in methylene chloride solution. We have been unable to detect any change in the nature of the catalyst during the course of the dimerisation of norbornadiene and have recovered it in high yields at the completion of the reaction. Our kinetic studies have shown that at 33.8°C, $-d[NBD]/dt = k[NBD]^0 [catalyst]^1 [cocatalyst]^1$ where $k = 6.575 \times 10^2$ l mol^{-1} sec^{-1} and the activation energy $E_A = 38.58$ kcal mol^{-1}.

We have also investigated the effects of polynuclear carbonyl complexes of metals other than cobalt. Thus in the presence of $BF_3 \cdot Et_2O$ in dichloromethane solution at ca. 35°C, $(\eta\text{-}C_5H_5)_2Fe_2(CO)_4$ has little effect on norbornadiene, both $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ give unidentified products, and both $Mn_2(CO)_{10}$ and $(\eta\text{-}C_5H_5)_2Mo_2(CO)_6$ give a gelatinous mass.

References

1 G.N. Schrauzer, Adv. Catal., 18 (1968) 373.
2 P.A. Elder, B.H. Robinson and J. Simpson, J. Chem. Soc. Dalton Trans., (1975) 1771.
3 T. Kamijo, T. Kitamura, N. Sakamoto and T. Joh, J. Organometal. Chem., 54 (1973) 265.