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Preliminary communication

THE COBALT-CATALYSED DIMERISATION OF NORBORNADIENE (C_7H_8) TO BINOR-S. EVIDENCE AGAINST THE π-COMPLEX MULTICENTRE PROCESS

MARY ENNIS, RICHARD M. FOLEY and A.R. MANNING*
Department of Chemistry, University College, Dublin 4 (Ireland)
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Summary

Product ratios obtained from the dimerisation of (7-MeC_7H_7) using a $[(C_7H_8)_2Co_2(CO)_4]/[BF_3 \cdot OEt_2]$ catalyst system in dichloromethane, or the use of a catalyst prepared from $[(C_7H_8)_2Co_2(CO)_4]$ and I_2 without $[BF_3 \cdot OEt_2]$ are only consistent with a reaction scheme based on a mononuclear Co^I catalyst, and suggest that a π-complex multicentre process is not important.

Schrauzer et al. [1] first prepared Binor-S ($C_{14}H_{16}$) by the stereospecific dimerisation of norbornadiene (C_7H_8) using a catalyst containing two cobalt atoms with a Lewis acid cocatalyst. They suggested that the two metal centres were necessary to bring about this reaction and proposed a π-complex multicentre (PCM) mechanism with concerted formation of C—C single bonds and loss of the double bonds [1,2]. Subsequent studies have shown that other complexes are also catalysts for this dimerisation; most contain cobalt [3,4]. However, it has been suggested that two cobalt atoms are not necessary to bring about Binor-S formation [5]. No definite evidence was advanced for this particular point of view, but as a consequence of our studies, some of which are reported here, we have come to the conclusion that it is true. For a large majority of the fifty or so catalyst systems that we have studied, the true catalyst appears to contain only one cobalt atom. It is relevant that, as Schrock and Osborn have shown, the Rh^I-catalysed dimerisation of C_7H_8 to Binor-S almost certainly takes place on a single metal centre [6].

IR spectroscopic studies of the various reaction mixtures only rarely show evidence for replacement of CO or other ligands by C_7H_8 molecules, and then it is usually limited. Except for a relatively small decline in the intensities of $\nu(CO)$ absorption bands due to the catalyst, the spectra tend to remain unchanged throughout the dimerisation, and unchanged catalyst may be recovered, often in high yields, e.g. $[(Ph_2C_2)Co_2(CO)_6]$ [3]. These observations lead us to question the PCM mechanism, and our scepticism was reinforced by a consideration of the Co—Co separations involved with such catalysts as $[Hg\{Co(CO)_4\}_2]$ [7]. Here, the large diene—diene separations of ca. 5 Å in any reasonable intermediate species would tend to make C—C bond formation difficult. Consequently, we devoted our efforts towards a study of the catalyst where the PCM mechanism seemed most likely, [*cis*-$(C_7H_8)_2Co_2(CO)_4$] [8].

The course of action which we adopted was to dimerise $(7\text{-}MeC_7H_7)$ [9] with a $[(C_7H_8)_2Co_2(CO)_4]/[BF_3 \cdot OEt_2]$ catalyst. The PMC mechanism predicts that all of the (C_7H_8) should appear as Binor-S and the $(7\text{-}MeC_7H_7)$ as dimethyl Binor-S or $[(MeC_7H_7)_2Co_2(CO)_4]$ unless diene exchange takes place prior to dimerisation. Independent studies show that exchange is very limited or non-existent, and that both (C_7H_8) and $(7\text{-}MeC_7H_7)$ are dimerised at comparable rates by $[Co_2(CO)_8]/[BF_3 \cdot OEt_2]$. In dichloromethane solution at 32°C with a $[BF_3 \cdot OEt_2]$ cocatalyst, $[(C_7H_8)_2Co_2(CO)_4]$ and $(7\text{-}MeC_7H_7)$ give a mixture of Binor-S, methyl Binor-S and dimethyl Binor-S with various mol ratios of $[MeC_7H_7]/[C_7H_8]$ (as complex). Typically, when these were 2/1, the product mole ratios were 1.9/1.3/96.8 with only ca. 8% of the (C_7H_8) appearing in the products, the remainder is found as $[(C_7H_8)_2Co_2(CO)_4]$. No detectable amounts of $[(MeC_7H_7)_2Co_2(CO)_4]$ are formed. These observations suggest strongly that the PMC mechanism is making, at best, only an insignificant contribution to the diene dimerisation. This suspicion was confirmed by the use of [*trans*-(2,3-dimethylbutadiene)$_2$Co$_2$(CO)$_4$] as a catalyst with $[BF_3 \cdot OEt_2]$ cocatalyst. It is as effective as $[(C_7H_8)_2Co_2(CO)_4]/[BF_3 \cdot OEt_2]$ in the formation of Binor-S, but the IR spectrum of the reaction mixture shows that although some [(2,3-dimethylbutadiene)$_2$ Co$_2$(CO)$_4$] disappears during the reaction, no $[(C_7H_8)_2Co_2(CO)_4]$ is produced, as it would have to be if the PCM process was operating.

A plausible mechanism for the dimerisation of (C_7H_8) which is consistent with our observations involves a limited decomposition of $[(C_7H_8)_2Co_2(CO)_4]$ to a monocobalt species containing the $[(C_7H_8)Co]$ moiety. These then take up free $(7\text{-}MeC_7H_7)$ molecules to give methyl Binor-S and, subsequently, dimethyl Binor-S. The Binor-S may arise from the PMC process, by transfer of (C_7H_8) from one cobalt centre to the other during breakdown of the dicobalt complex to the catalyst, or from complete decomposition to free (C_7H_8). It is limited. This suggestion would account for the marked solvent dependence of this stereospecific catalytic dimerisation and the efficacy of chlorocarbons, especially dichloromethane. This is a particularly 'dirty' solvent which is difficult to purify and which, when pure, tends to give species which could oxidise the dicobalt complexes to Co^I derivatives, a reaction which would be facilitated by sunlight. The role of the boron trifluoride may be to bring about this oxidation in the same way as acids assist the oxidation of $[(\eta\text{-}C_5H_5)_2Fe_2(CO)_4]$ to $[(\eta\text{-}C_5H_5)Fe(CO)_2L]^+$ [10].

To test this hypothesis we prepared an unstable Co^I complex by the addition of iodine to a dichloromethane solution of $[(C_7H_8)_2Co_2(CO)_4]$ [11]. After 4 minutes the dicobalt compound had disappeared. Norbornadiene was added to the reaction mixture. It was completely dimerised to Binor-S within 3 minutes at room temperature in the absence of any cocatalyst.

We feel that this reaction provides good evidence for our suggested mechanism, and is inconsistent with any important contribution from a PMC process. The dimerisation is probably a metal-catalysed cationic polymerisation of norbornadiene. It should be noted that the formation of nortricyclene derivatives with their cyclopropyl rings is characteristic of the reaction of norbornadiene with electrophiles such as bromine (ref. 2 and references therein). The single Co^I catalytic centre clearly has the ability to align the two dimerising C_7H_8 molecules so that they give Binor-S rather than other possible dimers. This is an ability not possessed by many other catalysts, and may well be a consequence of the tendency of Co^I complexes to adopt a trigonal bipyramidal structure.

References

1 G.N. Schrauzer, B.N. Bastian and G. Fosselius, J. Amer. Chem. Soc., 88 (1966) 4890.
2 G.N. Schrauzer, Advan. Catalysis, 18 (1968) 373.
3 Mary Ennis and A.R. Manning, J. Organometal. Chem., 116 (1976) C31.
4 G.A. Catton, G.F.C. Jones, M.J. Mays and J.A.S. Howell, Inorg. Chim. Acta, 20 (1976) L41.
5 H.J. Langenbach, E. Keller and H. Vahrenkamp, Angew. Chem. (Intern. Ed.), 16 (1977) 188.
6 R.R. Schrock and J.A. Osborn, J. Amer. Chem. Soc., 93 (1971) 3089.
7 G.M. Sheldrick and R.N.F. Simpson, Chem. Commun., (1967) 1015.
8 P. McArdle and A.R. Manning, J. Chem. Soc. A, (1970) 2123.
9 P.R. Storey and S.R. Fahrenholtz, J. Org. Chem., 28 (1963) 1716.
10 B.D. Dombeck and R.J. Angelici, Inorg. Chim. Acta, 7 (1973) 345.
11 J. Newman and A.R. Manning, J. Chem. Soc. Dalton, (1973) 1593.