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Preliminary communication

CATALYTIC CYCLODIMERISATION OF BUTADIENE BY $CoCl(PPh_3)_3$

M.A. CAIRNS and J.F. NIXON
School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)
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Summary

$CoCl(PPh_3)_3$ acts as a catalyst for the cyclic dimerisation of butadiene to 1,5-cyclooctadiene and 4-vinyl-1-cyclohexene at 60°. $CoCl(PPh_3)_3$ reacts with trifluorophosphine at room temperature to form the hydride complex $CoH(PF_3)_3(PPh_3)$.

Whereas $RhCl(PPh_3)_3$ has been reported to form $RhCl(PPh_3)_2(C_4H_6)$ when treated with butadiene [1] at room temperature, a similar mixture of $CoCl(PPh_3)_3$ [2] and an excess of butadiene shows no evidence of reaction even after one week. On heating at 60°, however, the solution becomes red-brown and a blue solid is precipitated. Examination of the volatile products after three days shows the presence of a large proportion of butadiene dimers the main components being the cyclic dimers 1,5-cyclooctadiene (COD) and 4-vinyl-1-cyclohexene (VCH) approximately in the ratio of 3/2. The involatile residue contains a small amount of higher oligomers, free triphenylphosphine and $CoCl_2(PPh_3)_2$, but no isolable butadiene cobalt(I) species.

A more detailed investigation shows that initially only small amounts of VCH and an unidentified dimer (possibly divinylcyclobutane [3]) are formed, but subsequently the proportion of COD increases until it is the major component after about three days. The total conversion of butadiene to dimers is ca. 30% after one week. [Molar ratio (butadiene)/(Co) 40.4/1].

Treatment of $CoBr(PPh_3)_3$ with butadiene under similar conditions gives only a trace of the cyclic dimers although conversion is increased to about 12% when benzene is added to the mixture to increase the solubility of the cobalt species. Introduction of benzene to the $CoCl(PPh_3)_3$ system has very little effect on the rate or extent of dimerisation, but vinylcyclohexene becomes the major dimeric product for both the bromo and chloro compounds.

No detectable oligomerisation of isoprene by $CoCl(PPh_3)_3$ was observed at 60° and attempted codimerisation of butadiene and ethylene under similar conditions affords only the C_8H_{12} dimers . When pure butadiene is heated at 60° for one week no cyclic dimers are formed, only a small amount of sticky white polymer, indicating that thermal dimerisation [3] is not significant under the reaction conditions. Only a trace of VCH was detected using $CoCl_2(PPh_3)_2$ instead of $CoCl(PPh_3)_3$. Butadiene, in the presence of small amounts of the π-allylic complex $Co(\pi\text{-}C_4H_7)(C_4H_6)(PPh_3)$ under the same conditions gives a 70% conversion to various linear dimers, trimers and higher oligomers. Only polymerisation has previously been reported in the literature [4]. The main dimeric products are 5-methyl-1,3,6-heptatriene (87%) and 1,3,6-octatriene (10%) identified by their ^1H NMR spectra [5—7].

The preferential formation of cyclic C_8H_{12} dimers in the $CoCl(PPh_3)_3$—butadiene system is of particular interest since linear oligomerisation of butadiene has so far been the characteristic feature of all other organocobalt systems studied [8], e.g., using tri-π-allylcobalt [9], the cyclooctenyl complex $Co(\pi\text{-}C_8H_{13})(C_8H_{12})$ [10] and a variety of systems containing cobalt in a reduced state [5,6, 11—14]. The common intermediate species in the linear dimerisation of butadiene is thought to be the π-methylheptadienyl butadiene complex $Co(\pi\text{-}C_8H_{13})(C_4H_6)$ whose structure has been determined by X-ray crystallography [15]. This active catalyst arises from the insertion of butadiene into a cobalt—hydride bond followed by the insertion of a second butadiene molecule into the resulting π-allylic—cobalt bond. The last step can ultimately give methylheptatriene or octatriene, depending on the direction of insertion.

In reactions which afford linear dimers only trace amounts of VCH and COD have been detected [5, 11], suggesting that a completely different catalytic cobalt species is involved in the formation of the cyclic dimers. Wilke and coworkers [9, 16] have made an extensive study of the cyclic oligomerisation of dienes catalysed by nickel systems and by analogy with their results it is tentatively suggested that the $CoCl(PPh_3)_3$ complex may undergo decomposition to give a cobalt(0) triphenylphosphine species, which then coordinates two butadiene molecules in the di-π-allylic C_8 chain form which has been established in the nickel systems. Subsequent ring closure affords COD or VCH.

It is interesting to note that whereas $CoCl(PPh_3)_3$ readily forms the cobalt(II) triphenylphosphine complex $CoCl_2(PPh_3)_2$ by oxidation or disproportionation, no such behaviour occurs in the analogous rhodium(I) or iridium(I) compounds.

Although $CoCl(PPh_3)_3$ readily affords $CoCl(CO)_2(PPh_3)_2$ with carbon monoxide [2], it does not act as a catalyst for the decarbonylation of benzaldehyde at 60°. The corresponding reaction with trifluorophosphine at room temperature on the other hand, unexpectedly produces the hydrido complex $HCo(PF_3)_3(PPh_3)$ in 28% yield.

A cobalt hydride intermediate is suggested by the observation of benzene (ca. 10%) as the major volatile product from the pyrolysis of solid $CoCl(PPh_3)_3$ at 160° in vacuo. Benzene is known to be formed in the thermal decomposition of both $CoH(N_2)(PPh_3)_3$ [17] and $CoCH_3(PPh_3)_3$ [17, 18], and an intramolecular *ortho*-metallation has been postulated.

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