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# THE DIMERIZATION OF 1,3-DIENES WITH THE NICKEL-LIGAND CATALYST: EVIDENCE FOR A MULTI-STEP MECHANISM

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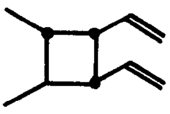
Butadiene is catalytically trimerized by zerovalent nickel to cyclododecatriene (CDT)[3)]. A multi-step mechanism for this reaction is generally accepted and is supported by the isolation of an intermediate $\alpha,\omega$-bis-$\pi$-allyl-$C_{12}$-nickel complex[4)]. Blocking one of the co-ordination sites on the nickel atom with a ligand (e.g. triarylphosphite or phosphine) produces a catalyst capable of dimerizing butadiene to a mixture of cycloocta-1,5-diene, cis-1,2-divinylcyclobutane, and 4-vinylcyclohexene[3,5)]. Two possible mechanisms have been suggested for this process:

a) a concerted process - modification of the Woodward-Hoffman rules to allow for interaction of the ligands with the metal indicate that this would be a symmetry allowed process[6,7)]

b) a multi-step process whereby the two butadiene molecules complex to the nickel atom and react together to form a $\pi$-allyl-$C_8$ chain which in a final step, under the influence of further butadiene, undergoes ring closure[3,8)].

The stereochemistry of the products formed by the dimerization and oligomerization of methyl substituted-1,3-dienes can, in many cases, only be explained by invoking a multi-step mechanism with rearrangement between the coupling step and ring closure[9)]. For example, the product obtained by the head-to-head dimerization of trans-piperylene is 1 and not 2 as would be expected in a concerted process.



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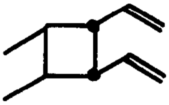

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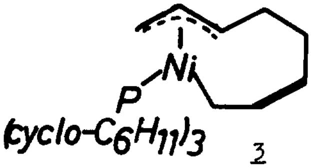

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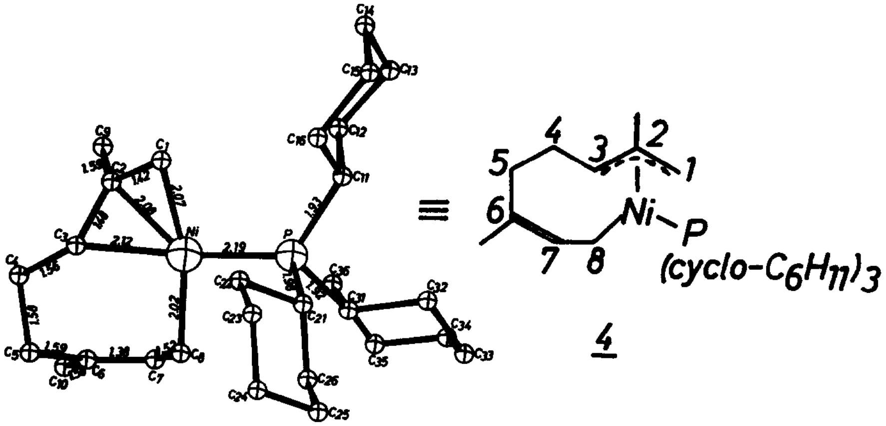
Furthermore a probable intermediate in the dimerization of butadiene has been isolated and assigned structure 3 on the basis of NMR evidence[10] (this assignement was later confirmed by other workers[11]).

We have now investigated the reactions of methyl substituted 1,3-dienes and report the structure of the product of the reaction with isoprene.

CDTNiPR$_3$ reacts with isoprene (where R = cyclo-$C_6H_{11}$ and $C_6H_5$), trans-piperylene (where R = cyclo-$C_6H_{11}$) and 2,3-dimethylbutadiene (where R = cyclo-$C_6H_{11}$) to give products in which the CDT molecule has been replaced by two diene molecules[12].

The structure of the bis-isoprene complex, $C_{10}H_{16}NiP$(cyclo-$C_6H_{11}$)$_3$, 4, has been determined by X-ray diffraction (Fig.). The compound crystallizes from ether as yellow plates (a = 16.711, b = 12.942, c = 12.339; β = 91.34; Z = 4; Space group $P2_1/n$). The structure has been determined by conventional means and refined to a provisional R factor of 0.12.



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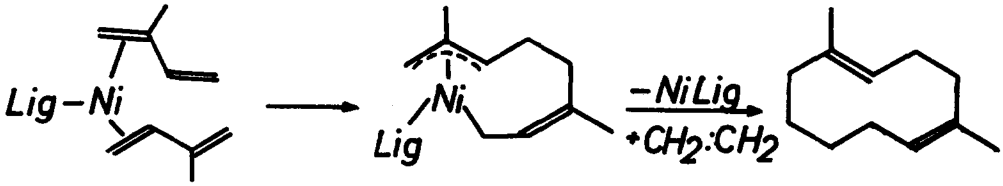
The geometry around the nickel atom is square planar: similar to that found in other $\pi$-allyl $NiCH_3.PR_3$ complexes$^{13)}$. The NMR spectrum of 4 ($\tau$ 4.20 (t, $C_7$-H), 7.30 (m, allylic-H), 7.59 (m, allylic-H), 8.23 (s, $CH_3$), 8.55 (s, $CH_3$), 8-9 (br, $C_6H_{11}$) in d-Benzene) indicates that the molecule has the same structure in solution as in the solid state (this has also been suggested for the corresponding "bis-butadiene" complex$^{11)}$). Noteworthy is the 2,6 position of the methyl groups. This arrangement suggests that before coupling the two isoprene molecules are not symmetrically bonded to the nickel atom (one possibility is 5). Analysis of the products of the oligomerization of two molecules of isoprene with one of ethylene, which gives 2,6-dimethyl-*cis,trans*-cyclodeca-1,5-diene (6) as the principal ten membered ring, indicates that this arrangement is also preferred in the nickel catalysed reactions$^{9,14)}$.



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Treatment of 4 in toluene with CO at -30° causes ring closure to give d,l-limonene in over 90% yield. In contrast the reaction with a triphenylphosphine melt gives isoprene in over 90% yield. Similar behaviour is observed in the reactions of the other bis-1,3-diene nickel complexes and of the "bis-butadiene" complex$^{10)}$. This ready cleavage of the $C_4$-$C_5$ bond has precedent in the reaction of *cis*-1,2-divinyl-cyclobutane with the nickel ligand system which, under favourable conditions, can give up to 30% butadiene$^{8)}$.

The results described above indicate that the catalytic dimerization of 1,3-dienes is almost certainly a multi-step process - at least in the case where the catalyst is the nickel-ligand system.

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