The Crystal and Molecular Structure of $CoC_{12}H_{19}$, a Catalyst for Butadiene Dimerization

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A COMPLEX with formula $CoC_{12}H_{19}$(I), m.p. 35·5°, has recently been obtained[1] by treating $CoCl_2$ with butadiene and $NaBH_4$ in alcohol; (I) is a catalyst for the dimerization of butadiene to 3-methylhepta-1,4,6-triene.

Our *X*-ray analysis has been carried out on single crystals of (I) held at about 0° in an inert atmosphere by the usual Weissenberg and multiple-film techniques, with visual estimation of the intensities. Crystallographic data: orthorhombic; $a = 13·16 \pm 0·04$; $b = 11·35 \pm 0·04$; $c + 7·30 \pm 0·03$ Å; space group $P2_12_12_1$, $Z = 4$; by starting with the three-dimensional Patterson synthesis, which allowed location of the Co atoms, the solution of the structure has been perfected through Fourier syntheses and 16 cycles of least-squares refinement; in the last 2 cycles anisotropic thermal factors were assigned to the all non-hydrogen atoms. The final value of the disagreement factor is 0·141 for **732** independently observed reflections, out of **799** observable reflections [(*hkl*) with *l* ranging from 0 to 5)].

The resulting molecular geometry is shown in Figure 1. Bond lengths and angles do not differ substantially from the values found in similar compounds (Table).[2] As expected,[3] the methyl-heptadienyl radical is π-co-ordinated to the metal
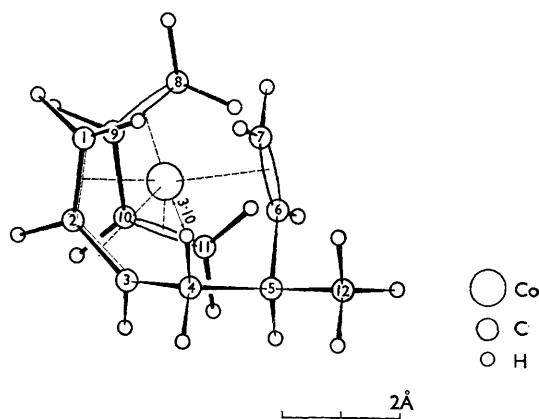

FIGURE 1. *Projection of the $CoC_{12}H_{19}$ molecule.*

via a terminal vinyl group [C(6)–C(7)] and an allylic portion, comprising atoms C(1)–C(2)–C(3) at the opposite end of the ligand. The butadiene group

TABLE

Intramolecular distances and bond angles ($\sigma_{C-C} \simeq 0{\cdot}038$; $\sigma_{Co-C} \simeq 0{\cdot}023$ Å; $\sigma_{<C-C-C} \simeq 1{\cdot}1°$)

Atoms	d (Å)	Atoms	d (Å)		
C(1)–C(2)	1·42	Co–C(1)	2·13	∠ C(1)–C(2) –C(3)	124·7°
C(2)–C(3)	1·37	Co–C(2)	1·99	∠ C(2)–C(3) –C(4)	126·5°
C(3)–C(4)	1·56	Co–C(3)	2·12	∠ C(3)–C(4) –C(5)	107·1°
C(4)–C(5)	1·55	Co–C(6)	2·10	∠ C(4)–C(5) –C(6)	107·1°
C(5)–C(6)	1·52	Co–C(7)	2·15	∠ C(5)–C(6) –C(7)	126·9°
C(6)–C(7)	1·32	Co–C(8)	2·11	∠ C(6)–C(5) –C(12)	108·9°
C(5)–C(12)	1·62	Co–C(9)	2·03	∠ C(4)–C(5) –C(12)	110·3°
C(8)–C(9)	1·43	Co–C(10)	2·04	∠ C(8)–C(9) –C(10)	119·0°
C(9)–C(10)	1·41	Co–C(11)	2·16	∠ C(9)–C(10)–C(11)	118·5°
C(10–C(11)	1·43				

is also π-co-ordinated in the usual *cis*-conformation.[3] Taking into account the experimental error, the C–C distances (see Table) do not differ significantly either within the allylic group (av. 1·39 Å) or within the butadiene ligand (av. 1·42 Å). Also comparison of the distances from Co to the C atoms of the π-co-ordinated groups, shows that the internal atoms of both the allylic and the butadiene groups are significantly closer than the others. The shortest distance from Co to H atoms linked to saturated carbon atoms is 3·10 Å and this suggests a possible electronic interaction between the metal and one of the hydrogen atoms bound to C(4).

If the allylic group is formally taken as a bidentate ligand,[2] the five-fold co-ordination around the Co atom may be roughly described as a distorted square pyramid, whose apex is in the middle of the vinyl group.

From the knowledge of the molecular structure and from the chemical evidence accumulated about (I),[1] a reasonable mechanism of butadiene dimerization, in agreement with that previously suggested,[1,3] is shown in Figure 2. In the step (A) → (B) a hydrogen atom migrates from C(4) to C(8) [or C(11)] (*cf.*, Figure 1) with the possible intermediate formation of a cobalt hydride; this is supported, in addition to chemical evidence,[3] by the short Co–H distance found. The metal co-ordination in (B) is nearly equivalent to that in (A): in fact, in the original complex the butadiene and the allylic groups are nearly parallel, one above and one below the Co atom, and the vinyl group is at about the same level as the Co atom. Furthermore, keeping the butenyl group in the *cis*-configuration, the H atom may readily return to the original position, as is required by the existence of the postulated chemical equilibrium between (A) and (B).[1] The second step [(B) → (C)] should include the displacement of the C(6)–C(7) vinyl end by a vinyl moiety of a butadiene molecule, the driving force
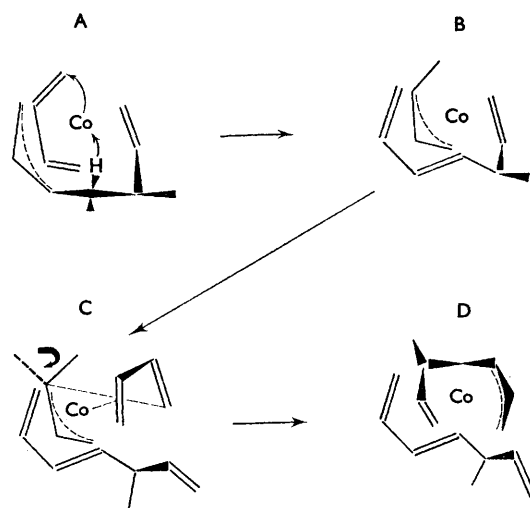

FIGURE 2. *Scheme showing the mechanism of butadiene dimerization. In* (A) *the same molecular orientation as in Figure 1 is assumed.*

residing in the greater tendency for the co-ordination of butadiene rather than an isolated vinyl group. Finally (D), the addition of the butadiene to the butenyl radical, proceeds through the rotation of the Me group *away* (for steric reasons) from the Co atom. The formation of a new methylheptadienyl radical takes place, which co-ordinates to Co with the same geometry as in (A), namely with the methyl group attached to the asymmetric C atom pointing in a direction opposite to Co. The *trans*-configuration of the central double bond found for methylheptatriene is also in agreement with this picture. A new butadiene group may now replace the methylheptatriene ligand. The restoration of the original complex, arising from the displacement of methylheptatriene by a

butadiene molecule, can take place at any of the (B), (C), or (D) steps of the reaction, but probably at (C) or (D), *i.e.*, after the displacement of the vinyl end of the methylheptatriene which was originally complexed with the cobalt atom.

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