Transition Metal Atoms as Catalysts: Oligomerisation of Butadiene Using Atoms of Ti, V, Cr, Mn, Fe, Co, or Ni

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Summary Co-condensation of atoms of the metals given in the title with butadiene and a cocatalyst such as $[\mathrm{Et_2AlCl}]_2$ in toluene causes the oligomerisation of butadiene; in some cases the cocatalyst is not necessary and addition of the metal atoms alone to butadiene in toluene causes efficient oligomerisation.

RECENTLY we described the preparation of $\mathrm{Ti(C_6H_6)_2}$.[1] Subsequently we have prepared bistoluene- and bismesitylenetitanium and found that they are generally very similar in their properties. The compounds $\mathrm{(RPh)_2Ti}$, R = H or Me, in liquid butadiene cause only trace polymerisation of butadiene solutions (Table 1). However, treatment of butadiene in toluene with $[\mathrm{EtAlCl_2}]_2$ and $\mathrm{(RPh)_2Ti}$ resulted in rapid oligomerisation of butadiene to cyclic trimers at room temperature. Since bisarenetitanium complexes are prepared by cocondensation of titanium vapour with the arene ligand we studied the cocondensation reaction between butadiene, $[\mathrm{EtAlCl_2}]_2$ in toluene (or benzene), and titanium atoms. The data in Table 1 shows that efficient oligomerisation occurs. More significantly, when an aliquot of the reaction mixture was treated with further excess of butadiene at room temperature then almost quantitative conversion into cyclododecatriene isomers is found.

TABLE 1. Reaction between metal atoms, butadiene, and $[\mathrm{Et_2AlCl}]_2$ in benzene (or toluene), and related studies

Catalytic system[a]	Conversion of butadiene/%	Temp/°, time/h	Oligomerisation products
$\mathrm{(C_6H_6)_2Ti}$	10	80, 6	polybutadiene
$\mathrm{(C_6H_6)_2Ti} + [\mathrm{Et_2AlCl}]_2$	100	60, 2	*ttt*-CDT (30%), *ctt*-CDT (67%), *cc*-COD (3%)
$\mathrm{Ti}_{atom} + [\mathrm{Et_2AlCl}]_2$[b]	100	20, 1	*ttt*-CDT (15%), *ctt*-CDT (80%), *cc*-COD (5%).
$\mathrm{V}_{atom} + [\mathrm{Et_2AlCl}]_2$	43	40, 3	*ctt*-CDT (30%), *ttt*-CDT (20%), COD (20%) linear trimers (three isomers) (30%)
$\mathrm{Cr}_{atom} + [\mathrm{Et_2AlCl}]_2$	60	60, 3	*ttt*-CDT (60%), *ctt*-CDT (35%), *cc*-COD (3%), linear trimers (2%)
$\mathrm{Mn}_{atom} + [\mathrm{Et_2AlCl}]_2$	40	50, 3	*ttt*-CDT- (35%), *ctt*-CDT (65%)
$\mathrm{Fe}_{atom} + [\mathrm{Et_2AlCl}]_2$[c]	100	20, 1	polybutadiene
$\mathrm{Co}_{atom} + [\mathrm{Et_2AlCl}]_2$[d]	10		linear dimers (80%), *cc*-COD 20%)
$\mathrm{Ni}_{atom} + [\mathrm{Et_8AlCl}]_2$[c]	90	60, 2	polybutadiene

[a] In a typical experiment the metal vapour (0·2—0·3 g) was co-condensed with butadiene (5—8 g) and $[\mathrm{Et_2AlCl}]_2$ (0·7—1 g) in benzene (or toluene) (50 cc) over 30—40 minutes. The reaction mixture was warmed to room temperature and then extracted and further treated as described in column 3 above. Volatile products were analysed using g.l.c.: *t trans*, *c cis*, CDT cyclododeca-1,5,9-triene, COD cyclo-octa-1,5-diene, VCH vinylcyclohexene. [b] Aliquots (5 ml) of the reaction mixture were treated with butadiene *ca.* 10 g) in sealed tubes at 50° giving almost quantitative conversion into cyclododecatrienes. We estimate that one gram of Ti in this system converts 1000 g of butadiene into CDT isomers. [c] Analysis of the reaction mixture immediately after warming the co-condensate showed (*ca.* 20%) linear and cyclic dimers and trimers to be present. [d] Not heated further.

Following this observation, we have studied the oligimerisation products of reaction between butadiene, $[\mathrm{Et_2AlCl}]_2$ in toluene (or benzene) with the atoms of V, Cr, Mn, Fe, Co, Ni. The products given in Table 1 show that oligomerisation or polymerisation of butadiene is observed in all cases, to varying extents.

We have also investigated the oligomerisation products formed by cocondensation of the atoms of Ti, V, Cr, Mn, Fe, Co, Ni with butadiene in toluene (or benzene) in the absence of $[\mathrm{Et_2AlCl}]_2$. The data in Table 2 shows that Ti atoms are inactive, whilst Co and Mn give essentially the same oligomers as when $[\mathrm{Et_2AlCl}]_2$ is present. Also, Ni and Fe give trimers rather than polymers whilst the reverse is true for V and Cr. Further, when an aliquot of the

TABLE 2. Reactions between metal atoms and butadiene in benzene[a]

Metal atoms	Conversion of butadiene / %	Temp/°, time/h	Products
Ti	*ca.* 0	—	—
V	44	50, 4	*ttt*-CDT (10%), *ctt*-CDT (15%) high oligomers (75%)
Cr	62	60, 6	isomers CDT (10%), high oligomers (90%)
Fe[b]	90	50, 2	linear trimers (63%), *ctt*-CDT (30%), *cc*-COD (7%)
Co	88	60, 2	linear dimers (69%), *cc*-COD (22%), traces of trimers (2—3%), high oligomers
Ni[b]	75	80, 2	*ttt*-CDT (45%), *cc*-COD (55%)
Ti + Al	*ca.* 0	—	—
Ti + At + EtCl ..	45	50, 2	*ctt*-CDT (45%), butenylbenzene (two isomers) (55%)
Ti + $\mathrm{Et_3Al}$	85	20, 2	polybutadiene
Ni + $\mathrm{Ph_3P}$[b]	100	60, 3	*cc*-COD (70%), VCH (25%) CDT (5%)

[a] Experiments were carried out as described in footnote (a) in Table 1. [b] Aliquots (5 ml) of the reaction mixture were treated with butadiene (*ca.* 10 g) in sealed tubes at 50° (Fe) or 85° (Ni) giving almost quantitative conversion, into the same products.

reaction mixture formed from Fe atoms, and butadiene in benzene was treated with excess of fresh butadiene then rapid oligomerisation occurred (Table 2).

Skell has shown that cocondensation of Mg atoms with alkyl halides forms Grignard reagents.[2] It would therefore be expected that cocondensation of Al atoms with alkyl halides would also form alkylaluminium halides. Accordingly we studied the products from effectively simultaneous cocondensation of Ti and Al atoms into a solution of butadiene and ethyl chloride in toluene. The data (Table 2) shows that again oligomerisation products are formed, together with products resulting from Friedel–Crafts alkylation of the aromatic solvent.

If the above experiment is carried out in the absence of ethyl chloride then no significant oligomerisation occurs. Thus, it appears that only when Ti, Al, and Cl are present in the reaction mixture are cyclic oligomers formed. When triethylaluminium is used instead of $[Et_2AlCl]_2$ then the butadiene is polymerised (Table 2). Finally, when Ni atoms are co-condensed into a mixture of butadiene and triphenylphosphine in benzene then cyclic dimers are formed almost exclusively.

It seems that the above cocondensation techniques using metal atoms provide a rapid and convenient method of looking for catalytic systems and, in some cases, for establishing which atoms are required for a particular reaction. For example, it is interesting that Fe atoms alone cause efficient oligomerisation of butadiene. Also, the observation of cyclic oligomerisation of butadiene by V is, we believe, the first example of such a reaction by this metal. Presently, we have little evidence concerning the nature of the catalytic species in these reactions. However, we note that low-temperature cocondensation of butadiene with certain metal atoms under a variety of conditions has lead to isolation of a number of zero-valent metal–butadiene complexes.[3] The apparatus used for this work is essentially that described previously[1] except that the less volatile components were introduced as a fine dispersion using a rotary 'atomiser' device.

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