Catalytic Oligomerisation of Butadiene using Catalysts derived directly from Metal Atoms or Di(η-arene)titanium Compounds

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The catalytic activity towards butadiene oligomerisation of zerovalent di(η-arene)titanium compounds has been explored under a variety of conditions. Co-condensations of metal atoms from the vapours of Ti, V, Cr, Mn, Fe, Co, or Ni with butadiene in benzene show that oligomerisation of butadiene is catalysed by all these metal atoms except titanium. Similar experiments, in which co-catalysts such as alkylaluminium halides or ligands such as tertiary phosphines are also present, have also been made. It is shown that the additional ligand or co-catalyst may change the nature of the oligomerisation product.

THE oligomerisation of butadiene to a variety of cyclic dimers or trimers, to linear dimers or trimers, or to higher oligomers has been found using many different transition-metal systems. Detailed studies on the catalytic oligomerisation of butadiene by nickel[1] have provided substantial evidence for the mechanism of these reactions. They proceed in a cyclic system *via* complex equilibria involving several intermediate compounds. It is a common feature of such cyclic catalytic systems that the monomers attach themselves to the metal centre, then undergo assembly, and finally depart as the oligomer. It is clear that the cyclotrimerisation of butadiene may involve at one time the co-ordination of three butadiene units to the metal. This in turn implies that a substantial portion of the co-ordination sphere of the metal atom is available to the butadiene ligands, so that none or few other ligands are irreversibly attached to the metal as the catalysis proceeds. Wilke[1] used the term ' naked nickel ' to indicate the role of the metal in the catalytic cyclotrimerisation of butadiene to cyclododecatrienes (cdt). This evocative phrase suggests that metal atoms themselves ought to be a source of catalyst systems. This paper describes studies on the co-condensation of transition-metal atoms with butadiene under a variety of conditions and the catalytic activity of the resulting solutions. The ability of di(η-arene)titanium compounds to act as catalysts for butadiene oligomerisation is also discussed.

RESULTS

Chemical Studies.—The co-condensation of titanium atoms with benzene or toluene at 77 K gave di(η-arene)-titanium complexes [$(RC_6H_5)_2Ti$] (R = H or Me).[2] Since these compounds readily decompose to the metal, and may therefore be regarded as a potential source of titanium atoms, they were treated with butadiene in benzene. Surprisingly, only trace polymerisation of butadiene was observed. However, addition of diethylaluminium chloride dimer to the mixture caused rapid and essentially quantitative conversion of butadiene to cyclic trimers (Table 1). The reactivity of butadiene with di(η-arene)titanium compounds together with different co-catalysts has been explored and the data (Table 1) show that [$(Et_2AlCl)_2$], [$(Me_2AlCl)_2$], and [$(EtAlCl_2)_2$] gave similar trimers whereas [$(AlCl_3)_2$] also gave polymers together with a small amount

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[1] G. Wilke, *Angew. Chem. Internat. Edn.*, 1963, **2**, 105.

[2] F. W. S. Benfield, M. L. H. Green, J. S. Ogden, and D. Young, *J.C.S. Chem. Comm.*, 1973, 866.

TABLE 1

Catalytic activity of the system [(arene)$_2$Ti] and [R$_n$AlCl$_{3-n}$] in butadiene oligomerisation (arene = C_6H_6 or MeC_6H_5; R = Me or Et; n = 0—3) and related studies [a]

System [b]	Conversion of bd/%	Conditions (θ_c/°C, t/h)	Distribution of products: *trans,trans,trans*-cdt	*cis,trans,trans*-cdt	ddt	cod	pbd	bb
[$(H_6C_6)_2Ti$]	10	80, 6					10	
[$(H_6C_6)_2Ti$] + [Et_2AlCl] [c]	100	60, 2	30	67		3		
[$(H_6C_6)_2Ti$] + [$EtAlCl_2$] [d]	100	70, 2	5	95				
[$(H_6C_6)_2Ti$] + $AlCl_3$ [d]	100	60, 2	3	56		2	30	10
[$(MeC_6H_5)_2Ti$]	20	20, 72					100	
[$(MeC_6H_5)_2Ti$] + Et_3Al	20	60, 3					100	
[$(MeC_6H_5)_2Ti$] + [Et_2AlCl]	100	60, 2	27	69		4		
[$(MeC_6H_5)_2Ti$] + [$EtAlCl_2$]	100	60, 2	2	98				
[$(MeC_6H_5)_2Ti$] + [Me_2AlCl]	100	60, 2	50	43		7		
[$(MeC_6H_5)_2Ti$] + [Me_2AlCl] + cht	100	60, 2	34	40	24	2		
[$(MeC_6H_5)_2Ti$] + Et_2Zn	0	60, 2 [e]						
[$(MeC_6H_5)_2Ti$] + [EtMgBr]	*ca.* 5	20, 25d [f]						
[$(H_6C_6)_2V$]	0	60, 4						
[$(H_6C_6)_2V$] + [$EtAlCl_2$]	35	60, 3					100	

[a] bd = Buta-1,4-diene, cdt = cyclododeca-1,5,9-triene, ddt = dodecatetraene, cod = *cis,cis*-cyclo-octa-1,5-diene, pbd = polybutadiene, bb = butenylbenzenes (two isomers, $MeCH{:}CMe{\cdot}C_6H_5$ and $MeCH_2{\cdot}CH{:}CH{\cdot}C_6H_5$, present), and cht = cyclohepta-1,3,5-triene. [b] Benzene (or toluene) was always present in all the reactions described in Tables 1—6. In separate experiments, addition of [$(Et_2AlCl)_2$] to a solution of [$(MeC_6H_5)_2Ti$] in light petroleum immediately gave a violet solution which quickly precipitated metallic titanium and no catalytic activity was detected. Also, Ti, Mn, Fe, or Ni atoms were co-condensed with butadiene and hexane in the absence of arenes and alkylaluminium compounds, and the ensuing reaction mixtures were heated under the conditions given in Table 6. It was found that the reaction mixture containing Ti remained effectively inactive while those containing Mn, Fe, or Ni showed substantially reduced activity. Therefore the role of benzene (or toluene) in the catalysis is probably not simply just that of solvent. [c] Excess of [Et_2AlCl] gave the same products. [d] Excess of [$EtAlCl_2$] or $AlCl_3$ increased the proportion of pbd and alkylation products of the benzene solvent. A ratio of Ti : Al = 1 : 2 is desirable for oligomerisation; a ratio of 1 : 3 gave mainly polymer. [e] Slow decomposition of [$(MeC_6H_5)_2Ti$]. [f] Linear dimers and trimers of bd, cdt, and less volatile products.

TABLE 2

Catalytic activity of the system M(atom)–[Et$_n$AlCl$_{3-n}$]–bd–arene in butadiene oligomerisation and related studies (M = Ti, V, Cr, Mn, Fe, Co, or Ni; n = 2 or 3; arene = C_6H_6 or MeC_6H_5)

System	Conversion of bd/%	Conditions (θ_c/°C, t/h)	Distribution of products: *trans,trans,trans*-cdt	*cis,trans,trans*-cdt	cod	Linear trimers	Linear dimers	pbd
Ti + [Et_2AlCl] [a]	100	20, 1	15	80	5			
V + [Et_2AlCl]	43	70, 3	20	30	20	30 [b]		
Cr + [Et_2AlCl] [c]	60	60, 3	60	35	3	2		
Mn + [Et_2AlCl]	40	50, 3	35	65				
Fe + [Et_2AlCl] [d]	100	20, 1						100
Co + [Et_2AlCl] [e]	10				20		80	
Ni + [Et_2AlCl] [f]	90	60, 2						100
Ti + Et_3Al	85	20, 2						100
Cr + Et_3Al	55	60, 2	35	65				
Fe + Et_3Al [g]	100	20' 1						100
Ni + Et_3Al [h]	65	20, 4	90		7	3		
' TiO_2 ' + [Et_2AlCl] [i]	100	50, 1	13	84		3		
' TiO_2 ' + Et_3Al	0							
' NiO ' + Et_3Al	100	80, 1	76			24		

[a] Analysis of the reaction mixture immediately after warming the co-condensate showed 40—45% conversion of bd to *trans,trans,trans*-cdt (15), *cis,trans,trans*-cdt (80), and cod (5%), and after 30 min at room temperature there was quantitative conversion. Aliquot portions (5 cm^3) of the reaction mixture were treated with bd (10 g) in sealed tubes at 60 °C giving almost quantitative conversion to cyclododecatrienes. We estimate that 1 g of Ti in this system converts 1 000 g of bd to cdt isomers. Increasing the reaction temperature increased the proportion of *trans,trans,trans*-cdt formed; at 80 °C it had increased to 25%. [b] Three isomers. [c] Analysis of the reaction mixture after warming the co-condensate showed *ca.* 12% conversion of bd to *trans,trans,trans*-cdt (60), *cis,trans,trans*-cdt (30), cod (3), and linear trimers (17)%. No further linear trimerisation was detected after conversion at 60 °C. [d] Analysis of the reaction mixture immediately after warming the co-condensate showed *ca.* 20% conversion of bd to linear and cyclic dimers and trimers. [e] From analysis of the reaction mixture immediately after warming the co-condensate to room temperature; further heating was not undertaken. [f] Analysis of the reaction mixture after warming the co-condensate showed *ca.* 9% conversion of bd to mainly cdt and small amounts of cod. [g] Analysis of the reaction mixture immediately after warming the co-condensate showed *ca.* 10% conversion of bd to linear trimers and cdt. [h] Aliquot portions (5 cm^3) of the reaction mixture were treated with bd (*ca.* 10 g) in sealed tubes at 100 °C giving almost quantitative conversion to *trans,trans,trans*-cdt (70), *cis,trans,trans*-cdt (23), and cod and vch (7%) (vch = 3-vinylcyclohex-1-ene). [i] Aliquot portions (5 cm^3) of the reaction mixture were treated with bd (*ca.* 10 g) in sealed tubes at 70 °C to give almost quantitative conversion to *trans,trans,trans*-cdt (12), *cis,trans,trans*-cdt (84), and linear trimers (*ca.* 3%).

TABLE 3

Catalytic activity of the system M(atom)–Al(atom)–EtCl–bd–C_6H_6 in butadiene oligomerisation and related studies (M = Ti, V, Cr, Fe, or Ni)

			Distribution of products						
System [a]	Conversion of bd/%	Conditions (θ_c/°C, t/h)	*trans,trans,trans*-cdt	*cis,trans,trans*-cdt	cod	Linear trimers	Other oligomers	pbd	bb [b]
Ti + Al + EtCl	45	50, 2		45					55
V + Al + EtCl [c]	50	40, 3					100 [d]		
Cr + Al + EtCl [e]	10		6	24					70
Fe + Al + EtCl [f]	90	20, 6						100	
Ni + Al + EtCl	18	70, 3	65		35				
Fe + Al + C_6Cl_6 [e]	15			25		65			10
Al + $TiCl_4$ [e,g]	23								100 [h]
Ti + $TiCl_4$ [e,i]	20								100 [j]
' TiO_2 ' + ' Al_2O_3 ' + EtCl [e,k]	0								
Ti + EtCl [e]	0								
Al + EtCl [e]	*ca.* 5								100

[a] EtCl : M and Al : M in excess of 1 : 1 (up to 5 : 1). [b] Two isomers of butenylbenzene, MeCH:CMe·C_6H_5 and $MeCH_2$·CH:CH·C_6H_5, were formed from the system M + Al + EtCl + bd + C_6H_6. Their relative amounts varied from metal to metal. [c] Analysis of the reaction mixture after warming the co-condensate showed *ca.* 7% conversion of bd to *trans,trans,trans*-cdt (5), *cis,trans,trans*-cdt (13), and bb (82%). [d] The other oligomers were involatile liquids which could not be analysed by g.l.c. [e] From analysis of the reaction mixture immediately after warming the co-condensate to room temperature; further heating was not undertaken. [f] Analysis of the reaction mixture after warming the co-condensate showed *ca.* 10% conversion of bd to *trans,trans,trans*-cdt (10), *cis,trans,trans*-cdt (15), and bb (75%). [g] Al : $TiCl_4$ *ca.* 10 : 1. [h] Consists of MeCH:CMe·C_6H_5, $MeCH_2$·CH:CH·C_6H_5, and *o*- and *p*-dibutenylbenzenes. [i] Ti : $TiCl_4$ *ca.* 1 : 1. [j] Consists of MeCH:CMe·C_6H_5 and $MeCH_2$·CH:CH·C_6H_5 identified by comparison with the products from the reaction $AlCl_3$ + bd + C_6H_6. [k] The predominant species in the vapour over Al_2O_3 were Al, Al_2O, and AlO.[5]

TABLE 4

Catalytic activity of the system M(atom)–Al(atom)–bd–C_6H_6 in butadiene oligomerisation (M = Ti, Mn, Fe, or Ni)

			Product distribution					
System	% Conversion of bd	Conditions (θ_c/°C, t/h)	*trans,trans,trans*-cdt	*cis,trans,trans*-cdt	ddt	cod	vch	bb
Ti + Al	0							
Mn + Al	45	60, 2	30	70				
Fe + Al [a]	20			18	60 [b]	22		
Ni + Al	70	90, 2	40			45	15	
Al	Trace							100

[a] An aliquot portion (10 cm^3) of the reaction mixture was treated with bd (*ca.* 3 g) in a sealed tube at 55 °C for 4 h giving 40% conversion to *cis,trans,trans*-cdt (30), ddt (63),[b] and cod (7%). [b] Three isomers.

TABLE 5

Catalytic activity of the system M(atom)–bd–MeC_6H_5 in the presence of other ligands

			Products						
System [a]	Conversion of bd/%	Conditions (θ_c/°C, t/h)	*trans,trans,trans*-cdt	*cis,trans,trans*-cdt	cod	vch	Linear trimers	Linear dimers	pbd
Ti + [Et_2AlCl] + PPh_3 [b]	100	40, 2	95	4					
' TiO_2 ' + PPh_3	0								
[' TiO_2 '] [c] + PPh_3	85	70, 3	27	65			7		
Cr + PPh_3	100	20, 4							100
Fe + PPh_3	37	50, 5						100	
Fe + $P(OPh)_3$	0								
Fe + P_4	10	50, 4	100						
Co + PPh_3	35	50, 5						100	
Co + $P(OPh)_3$	0								
Ni + PPh_3	100	60, 3	5		70	25			
Ni + $P(OPh)_3$	0								
Ni + P_4 [d]	73	70, 4	40	60					
' NiO ' + P_4 [d]	0 [e]								
Pd + PPh_3	0 [f]								
Pd + P_4 [d]	20	70, 3	Trace				100		

[a] M : L *ca.* 1 : 1. [b] Ti : PhP_3 : [Et_2AlCl] *ca.* 1 : 1 : 1. [c] [' TiO_2 '] Is an aliquot portion (5 cm^3) from the reaction mixture ' TiO_2 ' + [Et_2AlCl] + bd + MeC_6H_5 which was added to an equimolar amount of PPh_3 and bd (5 g) in MeC_6H_5. [d] Red phosphorus. [e] Metallic nickel was precipitated. [f] Some metallic palladium was precipitated, but higher ratios of PPh_3 : Pd resulted in formation of [$Pd(PPh_3)_4$] which was characterised by comparing its i.r. spectrum with that of an authentic sample. With excess of PPh_3 the reaction is stoicheiometric with respect to Pd co-condensed.

of Friedel–Crafts alkylation products such as butenylbenzenes. Excess of [$(Et_2AlCl)_2$] did not affect the products of butadiene oligomerisation. In contrast, excess of [$(EtAlCl_2)_2$] or [$(AlCl_3)_2$] caused increased polymerisation of butadiene and also alkylation of the aromatic solvents. For effective oligomerisation of butadiene these latter co-catalysts should be present in a ratio of less than 2 : 1 (Al : Ti). When [$(AlEt_3)_2$] was used as a co-catalyst only polybutadiene was formed.

Treatment of red toluene solutions of di(η-benzene)titanium with [$(Et_2AlCl)_2$] gave a violet solution immediately followed by formation of a red-brown solution and separation of a red-brown precipitate. The latter is extremely unstable to oxygen and water and could not be further purified or characterised. Treatment of the red-brown solutions with butadiene caused rapid cyclotrimerisation of butadiene to cdt. It was found that [$(EtAlCl_2)_2$] and [$(AlCl_3)_2$] reacted with [$(H_6C_6)_2Ti$] in an essentially identical manner to [$(Et_2AlCl)_2$]. In contrast, [$(Et_3Al)_2$] caused no change of colour of the [$(H_6C_6)_2Ti$] solution in toluene.

In a further attempt to isolate some intermediate titanium species the red-brown solutions from [$(Et_2AlCl)_2$] were treated with cycloheptatriene. A green solution formed, from which fine apple-green crystals separated. These are insoluble in hydrocarbon solvents and are decomposed by solvents such as ethers, CH_2Cl_2, and MeCN. However, they dissolved in an excess of [$(Et_2AlCl)_2$] in toluene and the resulting solution was very active indeed for the cyclotrimerisation of butadiene to cdt at room temperature. Hydrolysis of the green crystals resulted in evolution of ethane and a trace of butane. They were also shown to contain Ti, Al, and Cl. Painstaking attempts to grow green crystals of suitable size for crystal-structure determination were unrewarding but further study of this system is in progress.

Since the di(η-arene)titanium complexes were prepared directly from titanium atoms we investigated the co-condensation between titanium atoms, benzene, butadiene, and [$(Et_2AlCl)_2$]. It was found that a highly active catalytic system formed, giving essentially the same products as with di(η-arene)titanium. In view of the simplicity and facility with which atom co-condensation experiments may be carried out, we explored the catalytic activity of atoms of V, Cr, Mn, Fe, Co, or Ni when condensed with butadiene, benzene, and [$(Et_2AlCl)_2$] (Table 2). The data show that oligomerisation or polymerisation was observed for each metal, although the nature of the products and the isomer distribution was characteristic of individual atoms. These differences were shown to be replicable, indeed, every experiment given in Tables 1—6 was repeated at least once and the reproducibility of product yields and isomer distribution was within 10%.

It was also found that vaporisation of rutile (TiO_2), which gives mainly TiO and oxygen, also gave a highly active catalyst system for butadiene oligomerisation (Table 2). Also, the mixture formed by co-condensation of Ti atoms into [$(Et_2AlCl)_2$], butadiene, and toluene was warmed to room temperature and an aliquot portion was treated with a further excess of butadiene. The added butadiene was rapidly converted to cdt, together with a small proportion of cyclo-octadiene (cod). We estimate that by this method 1 g of titanium could cause conversion of *ca.* 1 000 g of butadiene to cyclododecatriene.

Skell [3] has shown that co-condensation of ethyl chloride with Mg atoms gives the corresponding Grignard reagent, RMgBr. It, therefore, seemed likely that Al atoms would react with EtCl forming alkylaluminium halides, in which case direct use of the inconveniently reactive alkylaluminium halides as co-catalysts might be avoided. Samples of Ti and Al metals were fused to form an alloy and the temperature was raised so that both Al and Ti atoms were evaporated into a mixture of butadiene, benzene, and ethyl chloride. The data (Table 3) show that oligomerisation of butadiene was indeed observed; however, a substantial quantity of butenylbenzenes was also formed under these conditions, suggesting that $AlCl_3$ was also a product of the reaction between Al atoms and EtCl. In a separate experiment it was shown that co-condensation of Ti atoms with butadiene, benzene, and $TiCl_4$ gave only mono- and di-butenylbenzenes, and similar products were formed when Al instead of Ti atoms were used. Following these observations we investigated the co-condensation of atoms of V, Cr, Fe, or Ni together with Al into butadiene, benzene, and EtCl (Table 3). With the exception of nickel, a marked reduction of cyclic products occurred and polybutadiene and butenylbenzene were formed in greater yields compared to the analogous experiments described in Table 2. Also, addition of Al atoms to butadiene, benzene, and EtCl gave a mixture of mono- and di-ethyl- and butenyl-benzenes.

Since we had no direct evidence concerning the role of EtCl in the experiments described in Table 3, we studied the co-condensation of atoms of Ti, Mn, Fe, or Ni together with Al atoms and butadiene in benzene in the absence of EtCl. The data in Table 4 show that, in the absence of EtCl, Ti atoms gave no catalytic activity. In contrast, Mn, Fe, or Ni behaved as if the Al atoms were not present (Table 6). In a separate experiment it was found that co-condensation of Al atoms with butadiene in benzene gave only traces of butenylbenzenes.

It is well established that the products of butadiene oligomerisation may be dramatically changed when a ligand, such as a tertiary phosphine or amine, is present in the reaction mixture.[4] We investigated the effect of added ligands under the conditions of the co-condensation experiments. The metal atoms were co-condensed with butadiene and benzene together with triphenylphosphine or triphenyl phosphite (Table 5). The data show that with Ni atoms the presence of PPh_3 caused a marked change of oligomerisation product, and cyclic dimers were the major products and only traces of cyclic trimers were found. This result precisely parallels the effect of tertiary phosphines in catalysis by nickel compounds (Table 7). Comparison of the data in Tables 5 and 6 shows that PPh_3 also caused modification of catalysis products by Fe or Co. Also addition of PPh_3 to the Ti atoms in a [$(Et_2AlCl)_2$] mixture caused a marked increase in selectivity of product and essentially quantitative conversion to 95% *trans,trans,trans*-cdt was achieved. Triphenyl phosphite blocked catalysis, whilst addition of red phosphorus to the Fe or Ni systems surprisingly caused an increase in the yields of cyclic trimers relative to dimers. We also observed that co-condensation of palladium with benzene, butadiene, and an excess of PPh_3 gave tetrakis(triphenylphosphine)palladium in good yield.

Finally, we studied the catalytic activity of atoms of Ti, V, Cr, Mn, Fe, Co, Ni, or Pd with butadiene in benzene

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[3] P. S. Skell and J. E. Girard, *J. Amer. Chem. Soc.*, 1972, **94**, 5518.

[4] R. Baker, *Chem. Rev.*, 1973, **73**, 487.

TABLE 6

Catalytic activity of the system M(atom)–bd–C_6H_6 (M = Ti, V, Cr, Mn, Fe, Co, Ni, or Pd) and related studies

			Distribution of products					
System	Conversion of bd/%	Conditions (θ_c/°C, t/h)	*trans,trans,trans*-cdt	*cis,trans,trans*-cdt	Linear trimers	cod	Linear dimers	Higher oligomers
Ti	0							
' TiO_2 '	0							
V [a]	44	50, 4	10	15				75
Cr [a]	62	60, 6	10					90
Mn	65	60, 4	35	60			5	
Fe [b]	90	50, 2		30	63	7		
' FeO '	0							
Co	88	60, 2	[c]			22	69	7
Ni [b]	75	80, 2	45			55		
' NiO '	65	70, 3	40	30	30			
Pd	42	70, 3			100 [d]			
Al	0 [e]							

[a] Analysis of the reaction mixture immediately after warming the co-condensate showed *ca.* 10% bd conversion to mainly cdt and only 10% higher oligomers. [b] Aliquot portions (5 cm^3) of the reaction mixture were treated with bd (*ca.* 10 g) in sealed tubes at 50 (Fe) or 85 °C (Ni) giving almost quantitative conversion to the same products as obtained from the original co-condensation reaction mixture. [c] Traces of trimers were also present. [d] Two isomers, ratio 15 : 1. [e] Traces of butenylbenzenes were detected.

TABLE 7

Some previously described butadiene-oligomerisation catalytic systems

Catalyst system	bd Conversion/%	Main product/%	Other products/%	Ref.
Titanium				
$TiCl_4$ + $[Et_2AlCl]$ (1 : 10) + C_6H_6	20.7 g [a]	*cis,trans,trans*-cdt (88.5)	*trans,trans,trans*-cdt (3), cod + vch (1.3), $>C_{12}$ [c] (8.2)	*b*
$TiCl_4$ + $[EtAlCl_2]$ + $[Et_2AlH]$ + PPh_3 (1 : 2 : 3 : 2) + C_6H_6	15.7 g [a]	*trans,trans,trans*-cdt (45.9)	*cis,trans,trans*-cdt (14), cod + vch (1.2), $>C_{12}$ (35.4), pbd (3.5)	*b*
$TiCl_4$ + $[Et_2AlCl]$ (2 : 1) + C_6H_6		pbd		*b*
Chromium				
$[\{(\eta\text{-}H_5C_3)CrI\}_2]$ + CH_2Cl_2	70	*trans,trans,trans*-cdt	*cis,trans,trans*-cdt (3 : 2)	8
$[Cr(pd)_3]$ + $[Me_3Al]$ or $[(\eta\text{-}H_5C_3)_3Cr]$		1,2-pbd		8
Manganese				
$[Mn(pd)_2]$ + PrMgCl (1 : 10) + Et_2O	34.3	*trans,trans,trans*-cdt (93.3)	vch (5.7), cod (1)	*d*
Ph_2Mn + thf	57 [g]	*trans,trans,trans*-cdt		*e*
Iron				
$FeCl_3$ + Al + $AlCl_3$ + C_6H_6	Not stated	cdt	Other trimers	*f*
$[(\eta^4\text{-cot})(\eta^6\text{-cot})Fe]$	Not stated	ddt	cod	12
$[(bipy)_2FeEt_2]$	90	cod (73)	vch (27)	*h*
$[Fe(CO)_2(NO)(\eta\text{-}C_3H_5)]$	>97	vch		*i*
$FeCl_3$ + Et_3Al + PPh_3	85	ot [j] (65)	mht [k] (30), Trimers (5)	13
$[Fe(pd)_3]$ + Et_3Al	82	pbd (62)	dt (24), Branched trimer (7), mht and other dimers	10
Cobalt				
$[(\eta\text{-}H_5C_3)_3Co]$	70	mht and ot (9 : 1) (38)	Linear trimers (34), $>C_{12}$ (28)	7
$Co_2(CO)_8$ + Et_3Al + C_6H_6	60	mht (90)	vch (8), ot (1)	*l*
$Co_2(CO)_8$ + Et_3Al + CH_2Cl_2 or $[\{(\eta\text{-}H_5C_3)_2CoI\}_2]$ + CH_2Cl_2		1,4-*cis*-pbd		*l*, 8
Nickel				
$[Ni(pd)_2]$ + $[Et_2Al(OEt)]$ (1 : 2)	100	*trans,trans,trans*-cdt (81.7)	*cis,cis,trans*-cdt (5.7), *cis,trans,trans*-cdt (4.8), cod (1.6), $>C_{12}$ (1.0)	11
$[Ni(pd)_2]$ + Et_3Al + $(o\text{-}PhC_6H_4O)_3P$ (1 : 2 : 1) or $[Ni(cod)_2]$ + $[Ni\{P(OH_4C_6Ph\text{-}o)_3\}_4]$ (3 : 1)	100	cod (96)	vch (3.1), cdt (0.2), $>C_{12}$ (0.2)	*m*
$[(\eta\text{-}H_5C_3)Ni(\mu\text{-}Br)_2AlBr_2]$		1,4-*trans*-pbd		8
Palladium				
$[(\eta\text{-}H_5C_3)_2Pd]$	40	ddt		8

[a] bd Converted per mmol of metal present in the catalytic system. [b] H. Breil, P. Heimbach, M. Kröner, H. Müller, and G. Wilke, *Makromol. Chem.*, 1963, **69**, 18. [c] $>C_{12}$ = Oligomers of bd higher than dimers or trimers. [d] A. Carbonaro, *Chimica e Industria*, 1973, **55**, 244. [e] R. L. Pruett and W. R. Myers, U.S.P. 3,372,206 (*Chem. Abs.*, 1968, **69**, 18,714). [f] H. Müller, D. Wittenberg, H. Seibt, and E. Scharf, *Angew. Chem. Internat. Edn.*, 1965, **4**, 327; H. Müller, G.P. 1,106,758 (*Chem. Abs.*, 1962, **56**, 2352E). [g] The reference states that 57% of the bd present was converted to *trans,trans,trans*-cdt. [h] A. Yamamoto, K. Morifiyi, S. Ikeda, T. Saito, Y. Uchida, and A. Misono, *J. Amer. Chem. Soc.*, 1968, **90**, 1878. [i] J. P. Candlin and W. H. Janes, *J. Chem. Soc.* (*A*), 1968, 1856. [j] ot = Octatrienes. [k] mht = Methylheptatrienes. [l] S. Otsuka, T. Kikuchi, and T. Taketomi, *J. Amer. Chem. Soc.*, 1963, **85**, 3709; S. Otsuka and K. Taketomi, *European Polymer J.*, 1966, **2**, 289. [m] W. Brenner, P. Heimbach, H.-J. Hey, E. W. Müller, and G. Wilke, *Annalen*, 1969, **727**, 161.

(Table 6). All these metal atoms gave rise to active catalytic systems except those of titanium. The inactivity of titanium was not surprising since di(η-benzene)titanium itself was essentially inactive. It was also found that, whereas vapours evaporated from TiO_2 or FeO did not cause butadiene oligomerisation, that from NiO acted similarly to Ni atoms (Table 6). Under the conditions of evaporation the main species present in these vapours were TiO,[5,6] Fe,[5] and Ni [5], respectively, and oxygen.

DISCUSSION

All catalysts or catalyst precursors for the oligomerisation of butadiene contain transition metals and they may be discrete metal compounds, such as [Ni(cod)$_2$],[7] [Ni(cdt)],[7] [Co(allyl)$_3$],[8] or [Cr(allyl)$_2$],[7] or mixtures of a metal compound and a reducing agent such as $RhCl_3$–EtOH [9] or [Fe(pd)$_2$]–Et_3Al (pd = pentane-2,4-dionate).[10] It is rare that the metal system initially added to butadiene retains any significant equilibrium concentration during the catalytic reactions. Normally the initial compound or system reacts with the butadiene, the metal enters the catalytic cycle, and some or all of the original ligands around the metal are lost. η-Cyclododecatrienenickel is one of the few well established compounds which is a member of the catalytic cycle and, as such, it is a true catalyst rather than a catalyst precursor.

Since true catalysts are highly reactive they are difficult to isolate or identify. Clearly, the nature of a catalyst precursor, whether it is a pure compound or a reaction mixture, may provide only circumstantial evidence of the nature of the true catalyst intermediates. Even the simple question of which atoms are necessary may be difficult to ascertain. It is normally an advantage of using a pure compound as catalyst precursor that the number of possible catalyst components is limited. For example, since [Ni(allyl)$_2$] [8] and [Ni(pd)$_2$]–Et_3Al [11] both cyclotrimerise butadiene to cdt it is clear that the components pd, Et, or Al are not essential to the catalytic cycle. In contrast, [Fe(cot)$_2$] [12] and [Fe(pd)$_2$]–Et_3Al [10] give different oligomerisation products showing that they do not give rise to the same true catalysts.

The role of first-row transition-metal atoms as catalysts for oligomerisation of butadiene under various conditions is summarised in the Tables 1—6. Table 7, which summarises some previously described catalyst systems containing the same metals, is provided for comparative purposes. Tables 1—6 contain a great deal of data and only those aspects which we feel are of greater significance are discussed here. Comparison of Table 6 with 7 shows, for example, that [Cr(allyl)$_3$],[8] [Co(allyl)$_3$], and [Fe(cot)$_2$] behave similarly to the metal atoms, and, therefore, may be assumed to be 'naked-atom' catalyst precursors. The systems Fe atoms–PPh_3 and $FeCl_3$–Et_3Al–PPh_3 [13] give identical oligomers, different from those given by Fe atoms alone, and this suggests that an Fe–PPh_3 unit is part of the catalytic cycle. It is perhaps unexpected that the catalytic activity of Cr and Co atoms is not changed by the presence of PPh_3.

The many experiments using Ti atoms lead to the conclusion that the atoms alone are inactive as cyclo-oligomerisation catalysts but that the presence of both Al and Cl atoms are sufficient for activity. Also, Mg may replace Al, with reduced activity. It is also interesting that the activity of the system Ti–[(Et_2AlCl)$_2$] may be modified by the presence of PPh_3 so that, as mentioned, it gives essentially complete conversion to 95% *trans,trans,trans*-cdt. The inactivity, as a catalyst, of Ti atoms or zerovalent Ti compounds is interesting and, in the light of the data on other transition-metal atoms (Table 6), rather unexpected. It is of interest to enquire how the co-catalyst causes the catalytic activity to increase. We observed that addition of [($EtAlCl_2$)$_2$] to di(η-benzene)molybdenum caused smooth oxidation to the cation $[(H_6C_6)_2Mo]^+$. Also, di(η-benzene)-vanadium in toluene will reduce [($EtAlCl_2$)$_2$] giving an Al mirror.[14] Di(η-benzene)chromium acts similarly.[15] Therefore, it might be that in the Ti system the added co-catalysts act as oxidising agents and are themselves reduced.

Prior to this work, no V catalysts for the oligomerisation of butadiene had been reported. However, we find moderate activity for this element. This demonstrates that metal-vapour techniques provide a rapid and effective method for exploring new catalysts. The potential of metal vapours for the production of catalysts is further accentuated by the observation that we were able to take aliquot portions of the co-condensation mixtures and treat them with further excesses of butadiene and then achieve further rapid oligomerisation (see footnotes to Tables 2, 4, and 6).

It is of chemical and economic interest that we have been able to employ rutile (TiO_2) instead of Ti metal as source. It is known that TiO_2 decomposes at its m.p. (1 850 °C) to a mixture of lower oxides (TiO, Ti_2O_3, and Ti_3O_5). At 2 000 °C the main gaseous species above this mixture is TiO.[5,6] We assume that under the conditions of our experiments, essentially TiO vapour is co-condensed with the other reactants.

As discussed above, it is possible by using metal

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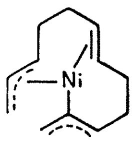
atoms as the source of the metal in a catalytic reaction to learn about the necessary constituents for catalytic activity. This apart, there is little evidence for the precise nature of the members of any given catalytic cycle. We note, however, that low-temperature co-condensations of butadiene with certain metal atoms under a variety of conditions has led to isolation of metal–butadiene complexes, such as tri(butadiene)tungsten and the molybdenum analogue,[16] a compound formulated as di(butadiene)nickel,[17] di(butadiene)carbonyliron and the monotrifluorophosphine derivative,[18,19] (butadiene)(toluene)iron,[18] and butadienetetracarbonylchromium [19] and the tetrakis(trifluorophosphine) analogue.[20] Also, treatment of nickel–butadiene co-condensates with excess of butadiene at −20 °C [17] gives the known true catalyst (I).[1,21]



(I)

Finally, we note that the experiments, where components of low volatility were introduced into the reaction vessel, would not have been possible without the development of the ' atomiser ' device described in the Experimental section.

EXPERIMENTAL

All experiments were carried out under nitrogen or argon or *in vacuo*. Crude butadiene was purified by distillation over potassium hydroxide pellets then molecular sieves (4A-XW). All solvents were distilled from calcium hydride immediately before use. Metal samples were used as supplied: titanium rod (0.5 in diameter) from Alfa Products, 99.6%; vanadium as premelted turnings from Alfa Products, 99.6%; chromium granules (Harrington Bros. Ltd.), 99%; manganese granules (B.D.H. Chemicals Ltd.), 99%; cobalt as premelted sponge (Koch-Light), 99.99%; nickel as premelted powder from Harrington Bros. Ltd.; aluminium rod (A.E.R.E., Harwell), 99.5%; and palladium powder (Johnson Matthey), 99%.

Reactions with butadiene at room temperature or above were carried out using sealed glass tubes containing *ca.* 25 cm^3 of reactants. Analyses by g.l.c. were made using a Pye–Unicam programmed instrument, model 14, with a flame-ionisation detector. Columns were packed with Apiezon (10%) on Embacel. The products were identified by coincidence of retention times with those of standard samples.

The apparatus for volatilisation of the metal and co-condensation of the vapours with reactants has been essentially described.[2] An additional feature in place of the vapour system was an ' atomiser ' device (Figure 1) for the introduction of reactant solutions containing involatile components. This consisted of a small electric motor (W. H. Models Ltd., Romford ' Bulldog ' 00 gauge) operating at up to 12 V which drove a rotating brass cone. The solution of the reactant was allowed to flow through a capillary onto the rotating shaft where it was rapidly spun as droplets from the rotating disc and deposited on the wall of the reaction vessel as a ' doughnut ' shaped ring [Figure 2(*a*)]. Since the reaction vessel was rotating, the ring of condensate swept out a film around the upper part of the reaction vessel where the metal atoms also impinged on the vessel wall [Figure 2(*b*)].

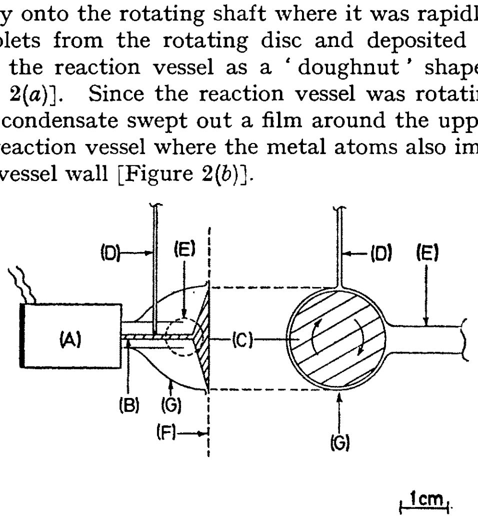


FIGURE 1 The rotary atomiser device: (A), electric motor and connections; (B), rotating drive shaft; (C), rotating disc; (D), solution inlet {*e.g.* [(Et$_2$AlCl)$_2$] in toluene}; (E), vapour inlet (*e.g.* butadiene and toluene); (F), atomised spray of microdroplets (and vapour beam); and (G), cowling. Rotating parts are hatched

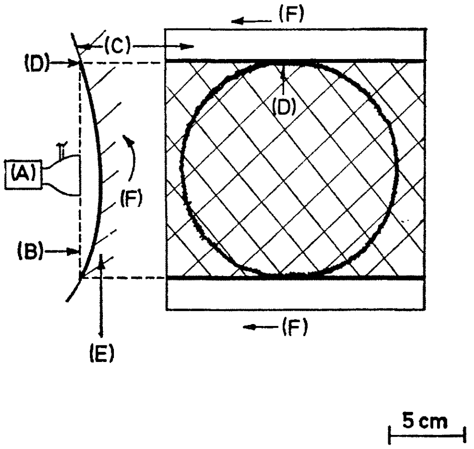


FIGURE 2 Condensation of atomised beam: (A), rotary atomiser device; (B), atomised beam of microdroplets; and (C), walls of evacuated vessel. (*a*) In stationary vessel: (D), atomised beam condensing as a circle on stationary vessel walls; (E), liquid-nitrogen coolant; and (F), no rotation. (*b*) In rotating vessel: (D), atomised beam condensing as a band (hatched area) due to rotation of vessel; and (F), rotation

Co-condensation of Metal Atoms into Butadiene, Benzene, and Diethylaluminium Chloride Dimer.—A typical reaction is described. A sample of massive metal (ideally 12.5 × 12.5 mm diameter rod) was placed on the copper hearth of the electron-beam furnace. The reaction vessel was evacuated and then rotated and placed in a liquid-nitrogen bath. A solution of butadiene (5—8 g) in benzene (or

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toluene) (50 cm^3) was introduced at a rate of *ca.* 100 cm^3 h^{-1}. A solution of [(Et$_2$AlCl)$_2$] (0.7—1.0 g) in toluene (10 cm^3) was concurrently introduced at *ca.* 20 cm^3 h^{-1}. The electron-beam gun was switched on and the accelerating voltage adjusted until evaporation of the metal was observed. Suitable rates for metal evaporation were *ca.* 500 mg h^{-1} and the conditions for this were found by trial and error assisted by knowledge of vapour pressure–temperature data for the metal in question.[22] Normally, little difficulty was experienced in gauging the rate of evaporation and, once the power input required had been determined, using the same power input in subsequent experiments gave a repeatable evaporation rate within *ca.* 10%. For example, an evaporation rate of *ca.* 500 mg h^{-1} could be obtained repeatably for Ti from a power input of 300 W. A clear indication of the volatilisation rate of the metal could be obtained by the build-up of the colour of the deposit on the walls of the vessel. The quantity of metal evaporated was estimated by weight loss from the furnace. However, in many reactions small quantities of massive metal were found in the reaction mixture, and also there was no evidence for the nature of the various metal products formed in the reaction solutions. Therefore, only an estimate of the stoicheiometry of these reactions may be made in terms of a probable upper limit of metal in the solution. The metal vapour and reactant solutions were co-condensed until it was judged that a suitable quantity of metal had been evaporated. Typically, the reaction was allowed to proceed for 30—40 min. The co-condensate, which was normally coloured, was allowed to warm to room temperature. The resulting solution was often viscous and was most conveniently removed by directly attaching a Schlenk vessel to the exit of the reaction vessel. On rotation of the reaction vessel the solution gradually transferred from its metastable position to the lower Schlenk vessel (see Figure 3). Subsequently, the volatile products were analysed either immediately or after being allowed to stand at various temperatures for some time. The particular conditions for each experiment are given in the Tables 1—6.

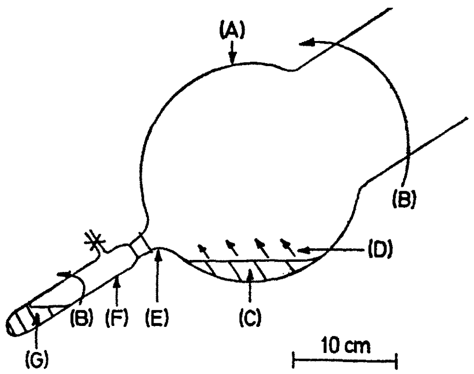

FIGURE 3 Extraction of reaction mixture: (A), vessel filled with inert gas (N$_2$ or Ar); (B), rotation; (C), reaction mixture formed from warming the co-condensate to room temperature; (D), thin film of reaction mixture carried round the surface of the vessel due to rotation and flowing into (F); (E), product outlet; (F), side-arm test-tube filled with inert gas (N$_2$ or Ar); and (G), reaction mixture collecting in (F)

Reaction between Di(η-arene)titanium Compounds and Butadiene.—A typical experiment is described. Di(η-benzene)titanium (0.05 g) was treated with [(Et$_2$AlCl)$_2$] (0.2 g) and butadiene (3 g) in toluene (5 cm^3) in a sealed glass tube. The mixture was warmed to 60 °C for 2 h, and, after cooling to room temperature, the mixture was analysed (g.l.c.). Details for related reactions are given in Table 1.

[4/2541 *Received, 7th December,* 1974]

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