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CATALYTIC REACTIONS INVOLVING BUTADIENE

III. OLIGOMERISATION WITH CATIONIC BIS(TRIPHENYLPHOSPHINE)(η^3-ALLYL) COMPLEXES

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Summary

The bis(triphenylphosphine)(η^3-crotyl)nickel cation is a catalyst precursor for the oligomerisation of butadiene to cyclic or linear dimers. Polymers and oligomers are also produced in variable amounts. The product distributions depend strongly on the type of solvent used and on the nature of co-catalysts. In the aprotic polar solvent DMF, the starting complex undergoes disproportionation, leading finally to a zerovalent nickel-phosphine catalyst. In protic solvents (alcohols) a cationic hydridonickel-phosphine catalyst is produced, but addition of sodium methoxide induces the formation of the zerovalent nickel-phosphine, therefore accounting for the changes in product selectivities.

Introduction

Cationic complexes of Group VIII transition metals have been found to have higher catalytic activities than neutral species, especially in the hydrogenation of unsatured substrates [1]. However, the use of cationic complexes in oligomerisation and/or polymerisation reactions has been reported in only few instances. The presence of a positive charge as well as the coordination of specific ligands on the metal centre can induce cationic oligomerisation and/or polymerisation of unsatured hydrocarbons. Butadiene can be polymerised into *trans*-1,4-polybutadiene in the presence of $\{\eta^3\text{-}C_4H_7)Ni(P(OEt)_3)_2\}PF_6$ [2]. The iron dinitrosyl cations $\{Fe(NO)_2S_n\}^+$ have been reported to be versatile catalysts for the polymerisation of styrene [3,4] and oligomerisation of isoprene, norbornadiene and phenylacetylene [3]. More recently, solvated nickel species such as $\{\eta^3\text{-}C_3H_5Ni(MeCN)_2\}PF_6$ [5] and the

* For part II see Ref. 17; also paper V in the series of cationic η^3-allyl complexes, for part IV see Ref. 18.

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palladium(II) solvate $\{Pd(MeCN)_4\}(BF_4)_2$ [6] were found to induce the oligomerisation of alkenes and dienes.

Recently [7], we described a convenient way of preparing cationic η^3-allyl complexes starting from tetracarbonylnickel or bis(1,5-cyclooctadiene)nickel and allyloxyphosphonium **1** or allylthiouronium **2** salts according to equations 1 and 2. Since the intermediacy of η^3-allylnickel has been demonstrated in numerous exam-

$$\underset{\textbf{(1)}}{\{RC_3H_4\overset{+}{O}P(NMe_2)_3\}Y^-} + NiL'_n \xrightarrow{2L} \underset{\textbf{(2)}}{\{(\eta^3 - RC_3H_4)NiL_2\}^+Y^-} + O{=}P(NMe_2)_3$$

$$(L'_n = 4CO,\ 2\ 1,5\text{-COD};\ L = R_3P,\ (RO)_3P) \qquad (1)$$

$$\underset{\textbf{(3)}}{\{RC_3H_4\overset{+}{S}C(NMe_2)_2\}Y^-} + Ni(CO)_4 \xrightarrow{SC(NMe_2)_2} \underset{\textbf{(4)}}{\{(\eta^3\text{-}RC_3H_4)NiSC(NMe_2)_2\}^+Y^-} \qquad (2)$$

ples of catalytic C–C bond formation involving butadiene [8], we have investigated the ability of complexes **3** and **4** to induce catalytic oligomerisation of butadiene. The product pattern depends strongly on the nature of the solvent used in the reactions, and can be explained in terms of important modifications of the coordination sphere and/or of the oxidation state of nickel.

Results and discussion

All catalytic runs were performed with 0.5 m*M* of the cationic complexes **2a** ($L = PPh_3$) and **4** in 100 m*M* of solvent at temperatures between 60 and 120°C for reaction times between 5 and 20 h. However, no catalytic activity was observed for **4**, and so systematic studies were undertaken only with **2a**. The products were separated into two parts by distillation under high vacuum. The distillate contains products up to C_{20}, mainly dimers and trimers. The residue contains oligomers and polymers, which can be separated by their solubilities in acetone and toluene. Inspection of Tables 1–3, which summarize the most significant results, reveals the strong effect of the nature of the solvent and/or of the presence of a co-catalyst on the product distribution.

Reaction in aprotic media

In aprotic media, the light oligomers are mainly of the cyclic type e.g., 4-vinylcyclohexene (VCH) and 1,5-cyclooctadiene (1,5-COD) (Table 1). If the reaction is performed without a solvent or with non polar solvents such as toluene, dichloromethane or THF, large amounts of higher oligomers are formed. Noteworthy is the higher proportion of acetone-insoluble oligomers when neat butadiene or toluene is used. Preliminary GPC results on two fractions of such products are shown in Fig. 1. A marked binodal distribution is observed with toluene as solvent, whereas the use of dichloromethane gives rise to a practically uninodal distribution [9]. The use of more polar aprotic solvents leads to higher conversions of butadiene. The best results were obtained with DMF, higher turnover rates and better selectivities being

TABLE 1

OLIGOMERISATION OF 1,3-BUTADIENE IN APROTIC SOLVENTS [a]

Solvent	Butadiene (mM)	Reaction conditions		Butadiene conversion (%)	Turnover (h^{-1})	Product selectivity (%) [b]					
		Temp. (°C)	Time (h)			VCH	COD	CDT	others	Residue	
										Sol. acetone	Sol. toluene
–	324	80	5	0							
–	398	120	5	74	118	10	31	11	5	traces	43
Toluene	296	120	5	75	89	5	17	3	–	11	64
THF	256	120	5	74	76	12	41	11	2	23	11
Acetonitrile	324	120	5	38	49	21	39	14	2	24	0
DMF	314	80	5	96	121	15	40	20	2	23	0
DMF	342	120	5	92	126	18	50	17	–	15	0

[a] Reaction conditions used: 2a, 0.5 mM; solvent 100 mM. [b] VCH: 4-vinylcyclohexene; COD: 1,5-cyclooctadiene; CDT: cyclododecatrienes; others: octatrienes and traces of oligomers > C_{12}.

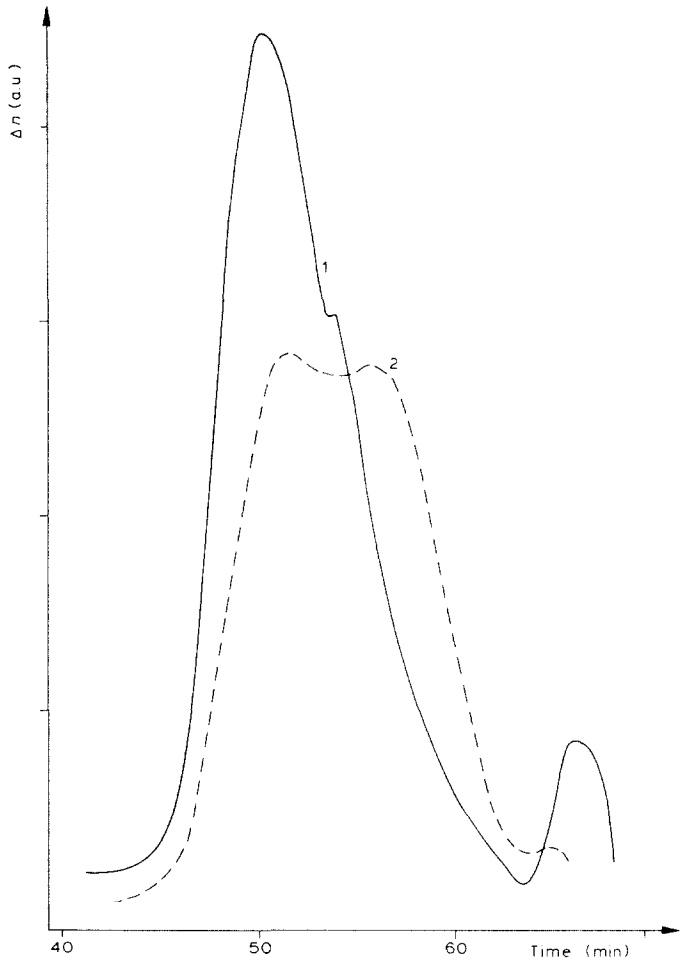


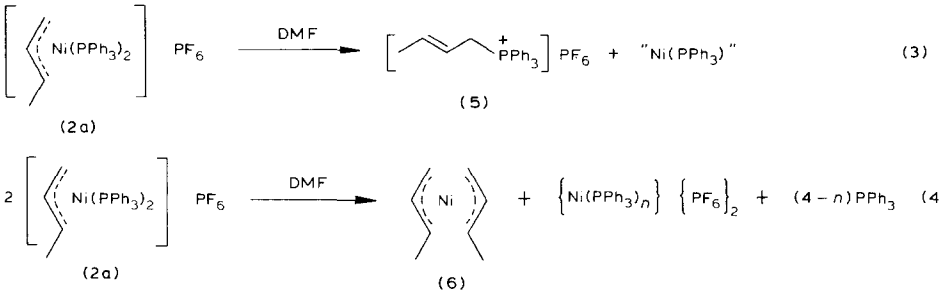
Fig. 1. Gel permeation chromatograms of butadiene oligomers produced in the reaction of butadiene (300 mM) with complex **2a** (0.5 mM) in dichloromethane (curve 1) and toluene (curve 2) for 5 h at 120°C.

observed even at lower temperatures. Polymers are no longer produced in this solvent. Mass spectrometric analysis of the mixture resulting from the hydrogenation of the acetone-soluble oligomers indicates the presence mainly of macrocyclic hydrocarbons.

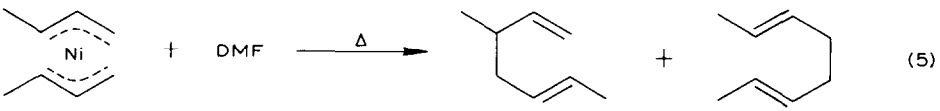
It is well established that only zerovalent nickel compounds are able to induce the catalytic cyclo-di- and -trimerisation of butadiene [8]. For example, use of the complex Ni(1,5-COD)$_2$ under the conditions gives cyclic trimers (Table 1). Thus it seems that the cationic complex **2a** in the presence of DMF gives rise to a zerovalent nickel compound e.g., Ni(PPh$_3$)$_n$.

Two reaction pathways can be envisaged for the formation of such compounds: (i) a nucleophilic attack of phosphine on the allyl ligand as in eq. 3, or (ii) a disproportionation leading to a bis(η^3-allyl) nickel compound and a cationic phosphine nickel complex, as in eq. 4.

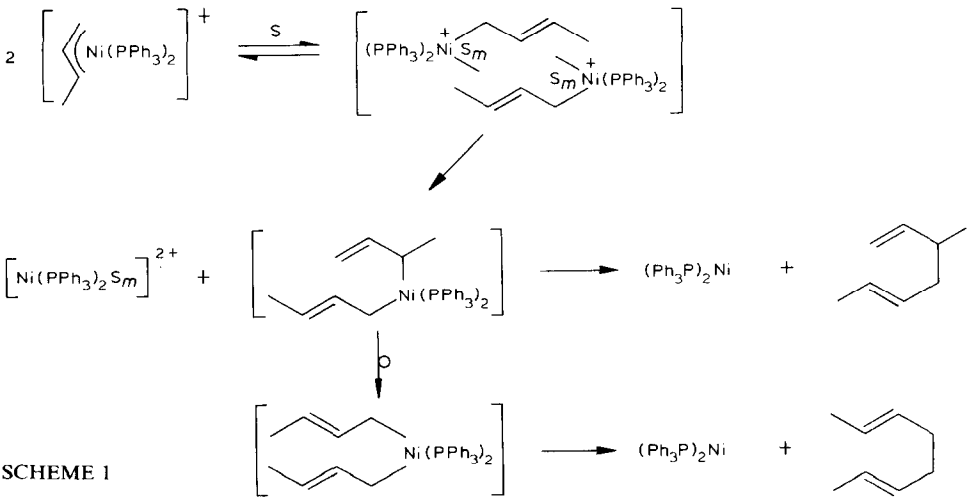
phine nickel complex, as in eq. 4.



Formation of allylphosphonium salts was observed during attempts to extend reaction 1 to the more basic tributyl- and tricyclohexyl-phosphine [10]. Disproportionations were reported by Wilke and his co-workers [11] for (η^3-allyl)nickel bromides in good donor solvents such as ethers, amines and amides. This reaction is also observed for cationic allylnickel complexes. Heating complex **2a** for a short period in DMF leads to the formation of 2,6-octadiene and 3-methyl-1,5-heptadiene (90% yield; 1/2.7 ratio) together with metallic nickel and nickel(II)-phosphine complexes. The isolation of the 1,5-dienes suggests that under the conditions used (80°C), the bis(η^3-crotyl)nickel formed in reaction 4 decomposes as shown in eq. 5. However, we have no evidence for the presence of **6** during the reaction. A



phosphine-containing analogue of **6** seems a more reasonable intermediate. In the light of the recent observations of Åkermark and Hegedus on allyl exchange [12] and of Jolly on reactions of bis(η^3-allyl) complexes with phosphines [13], we suggest Scheme 1 for the formation of zerovalent nickel species involved in the cyclo-oligomerisation of butadiene.



SCHEME 1

TABLE 2

OLIGOMERISATION OF 1,3-BUTADIENE IN PROTIC SOLVENTS [a]

Solvent	Butadiene (m*M*)	Reaction conditions		Butadiene conversion (%)	Turnover (h^{-1})	Product selectivity (%) [b]				
		T (°C)	Time (h)			1,3,7-OT	1,3,6-OT	Others	> C_{12}	Residue
										Sol. acetone / Sol. toluene
acetic acid	287	120	5	0						
methanol	315	80	5	36	45	22	31	–	–	23 / 23
methanol	277	120	5	48	53	19	37	–	8	19 / 17
methanol	324	120	20	55	18	7	27	–	7	23 / 36
methanol [c]	333	120	5	65	86	9	49	2	4	18 / 18
methanol [d]	333	120	5	49	65	9	32	–	8	15 / 35
i-propanol	305	80	5	74	90	13	64	10	0	/ 13
i-propanol	314	120	5	91	114	8	49	13	15	/ 15

[a] Reaction conditions used: **2a**, 0.5 m*M*; solvent, 100 m*M*. [b] 1,3,7-OT = 1,3,7-octatriene; 1,3,6-OT = 1,3,*cis*-6-octatriene; others: VCH, COD, CDT and telomers; > C_{12}: oligomers in the range C_{16}–C_{32}. [c] Trace amount of hydrogen. [d] 1 bar hydrogen.

TABLE 3

OLIGOMERISATION OF BUTADIENE IN METHANOL IN THE PRESENCE OF SODIUM METHOXIDE [a]

Methanol (m*M*)	Sodium methoxide (m*M*)	Butadiene (m*M*)	Reaction conditions		Butadiene conversion (%)	Turnover (h^{-1})	Product selectivity (%) [b]		
			T (°C)	Time (h)			1,3,6-OT	1,3,7-OT	Others
500	0.5	238	60	7	4.6	3	–	100	–
100	5	277	60	7	53	42	7	55	38
100	5	261	90	7	45	34	10	59	31

[a] **2a**: 0.5 m*M*. [b] Others: essentially 1-methoxy-2,7-octadiene and 3-methoxy-1,7-octadiene.

Under the catalytic conditions reaction 4 will also proceed rapidly since there is no evidence for an induction period. This disproportionation is easier in a good donor solvent than in a non-donor solvent such as toluene. In fact, use of toluene leads to intractable products.

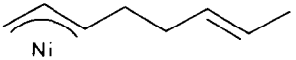
The presence of both cationic and zerovalent nickel species can account for the formation of macrocyclic oligomers by a route similar to that proposed by Miyake and his co-workers [14]. Finally, in the absence of coordinating solvents, the reaction mainly involves species derived from complex **2a** by dissociation of at least one phosphine ligand [2].

Reaction in protic media

In protic solvents such as alcohols, but not carboxylic acids (Table 2), the light oligomers obtained are mainly linear, e.g. 1,3,6-octatriene and 1,3,7-octatriene. The latter was isolated by preparative gas chromatography and shown to be the *cis* isomer. Noteworthy is the formation of significant amounts of linear oligomers in the C_{16}–C_{24} range, especially where isopropanol was used. GC/MS analysis of this hydrogenated fraction indicates the absence of cyclic products. However, linear and branched products are present, and attempts to improve the selectivity towards linear C_{16}–C_{24} compounds were unsuccessful. Use of lower temperatures suppressed the formation of these oligomers.

If the reaction is carried out under a low partial pressure of hydrogen (i.e. the autoclave is flushed with hydrogen prior to the catalytic run) the conversion of butadiene and the selectivity for octatrienes are increased. Addition of one equivalent of sodium methoxide practically inhibits the oligomerisation of butadiene (Table 3). However, as usual [8], the presence of an excess of this reducing agent leads to the conversion of butadiene, albeit in lower yield, into octatrienes and 1-methoxy-2,7-octadiene and 3-methoxy-1,7-octadiene. Noteworthy is the variation in selectivities observed for the dimers: 1,3,7-octatriene is now preferentially formed.

As pointed out by Jolly and Wilke [8], the linear oligomerisation of butadiene to octatrienes may proceed either through the initial formation of a bis(η-allyl)-C_8-nickel complex or through the addition of a nickel hydride species to butadiene followed by the insertion of a second molecule of butadiene into the η^3-crotyl–nickel bond. Indirect support for the latter mechanism was provided by the insertion of a butadiene molecule in the η^3-crotyl bond of $\{\eta^3\text{-}C_4H_7NiI\}_2$, giving rise to the octadienyl complex **7**, which was identified spectroscopically [15]. Under the condi-



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(7)

tions we used, the yields of 1,3,6-octatriene are noticeably higher than those of 1,3,7-octatriene, and the chain growth which leads to C_{16}–C_{20} products proceeds easily, especially where isopropanol is used as solvent. Both observations can be accounted for in terms of the participation of a species similar to **7**, and thus indicate the presence of nickel hydrides as catalysts. Such compounds can be formed (i) through hydride β-elimination from complex **2a** or a complex similar to **7** in which insertion of butadiene has occurred, or (ii) by nucleophilic attack of the

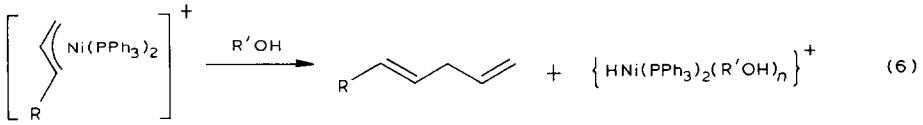
TABLE 4

ISOMERISATION OF 1-DODECENE IN THE PRESENCE OF COMPLEX **2a** [a]

Solvent (m*M*)	Initial hydrogen pressure (bar)	Reaction conditions		Conversion (%)	Turnover (h^{-1}) trans-2-	Extent of isomerisation [b] (%)	Product selectivity (%)				
		T (°C)	Time (h)				1-dodecene	cis-2-dodecene	dodecene	(cis + trans 3-dodecene	dodecane
DMF	0	120	22	12	0.5	12	88.4	5.1	6.3	–	0.2
DMF	5	120	22	88	3.6	61	12	24	35	2	27
Methanol	0	120	5	9.5	1.7	9	90.5	5.7	3.5	–	0.3
Methanol	0	120	22	16	0.6	15.5	84.3	9.5	6	–	0.2
Methanol	traces	120	5	20.5	3.5	19.5	79.5	10.7	7	1.9	1
Methanol	5	120	5	78	14	68	22	34	30	4	10
i-propanol	0	120	63	74.5	1.1	74	25.5	30	32.7	11.6	0.2

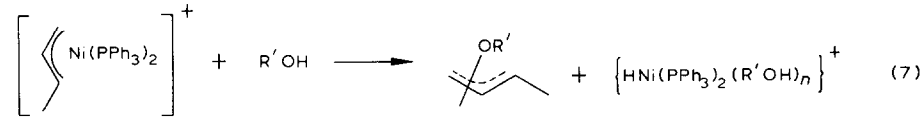
[a] Dodecene: 46 m*M*; **2a**: 0.5 m*M*. [b] The starting 1-dodecene contains 1.8% *cis*-2-dodecene, 1% *trans*-2-dodecene and 0.2% dodecane.

alcohol on the η^3-allyl ligand, as in eqs. 6 and 7. It is known that nickel hydrides are catalysts for the isomerisation of double bonds in alkene [16]. We found that



(6)

(R = H, $(C_4H_6)_m$; R' = Me, *i*-Pr)



(7)

complex **2a** in the presence of methanol or isopropanol is indeed, capable of isomerising 1-dodecene even in the absence of hydrogen (Table 4). If hydrogen is present in excess (5 bar), isomerisation and hydrogenation proceed readily, but the starting material is not recovered. Comparison with other isomerisation catalysts indicates that complex **2a** is not an efficient and selective catalyst, presumably because of the presence of two phosphine ligands in the nickel coordination sphere, and addition of triphenylphosphine to the reaction mixture does inhibit the reaction.

Addition of an excess of sodium methoxide to the catalyst suppresses the isomerisation. Correspondingly, in the presence of the reducing agent the oligomerisation of butadiene must take another course since the reaction occurs at a lower temperature and the 1,3,7-octatriene predominates over the 1,3,6-isomer. Therefore it can be assumed that under these conditions a pathway involving a bis(η-allyl)-C_8-nickel complex is now operative. Such a route will also account for the formation of the alkoxyoctadienes as by-products.

Experimental

All catalytic runs were performed in a 300 ml stainless steel autoclave equipped with gas inlets, heating and magnetic stirring. To avoid any effect of the metal surface, the reactions were carried out in a glass vessel attached to the internal wall of the autoclave. The starting complex [7] was weighed into the glass vessel and placed in the autoclave which was closed and submitted to several vacuum-argon cycles. Solvent was then introduced under argon.

Oligomerisation of 1,3-butadiene

The required amount of 1,3-butadiene was distilled from a pressure bottle into the cooled autoclave, and reaction was carried out under the conditions shown in the Tables.

The products were distilled and analysed by GC on several columns and identified by comparison with authentic samples and by GC/MS. The ratio of oligomers were determined by GC with n-decane and n-dodecane as internal standards for C_8 and C_{12} oligomers, respectively. The residues from distillation were

separated by using their solubilities in acetone and toluene. The higher oligomeric fractions (100 μl solution samples) were analyzed on three columns of Microstyragel (500, 10^4, 10^6 Å; 30 × 0.8 cm), elution being performed with THF (0.4 ml/min) and detection with a Waters R 401 refractometer [9].

Isomerisation of 1-dodecene

1-Dodecene (10 ml, 45 m*M*) was added to a solution of complex **2a** as indicated in Table 4. After reaction, the products were distilled and analyzed and identified by GC and GC/MS.

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