Main Stages of Unusual Allyl Coupling Involving Nickel Bis-η^3-Allyl Complexes in the Presence of Dichlorobutenes

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Abstract—The reactions of nickel bis-η^3-allyl complexes with dichlorobutenes were studied. The overall process includes several stages, each characterized by substantially different reactions: traditional allyl coupling, substrate insertion between recombining allyl ligands, and the trimerization of allyl fragments accompanied by hydride transfer (unusual allyl coupling). Unusual allyl coupling occurs at a final stage preceded by the formation of oligomeric nickel intermediates with the mean composition $Ni_4(C_3H_5)_6(C_4H_6)_3Cl_7$. Their decomposition gives nonadiene and nonatriene isomers and propene. Trace amounts of molecular hydrogen were found indicating the formation of nickel hydride complexes at the final stage. Nickel bis-η^3-allyl complexes react similarly with different dichlorobutenes.

INTRODUCTION

We have recently reported an unusual direction in the decomposition of bis-η^3-allylnickel in the presence of 1,4-dichlorobutene-2 (1,4-DCB-2) [1, 2]. Nonadiene and nonatriene isomers formed due to the trimerization of allyl fragments were observed along with the expected products of allyl coupling (hexadiene-1,5; 7-chloroheptadiene-1,5; and decatriene isomers). At the equimolar $Ni(C_3H_5)_2$: 1,4-DCB-2 ratio in diethyl ether, the overall yield of these compounds reaches 60–65% per allyl fragment. The unusual character of the reaction and its new opportunities for syntheses forced us to study this interaction and extend the range of reactants that might be used.

EXPERIMENTAL

Nickel bis-η^3-allyl complexes $Niall_2$ (all = C_3H_5, 1-CH_3–C_3H_4, and 2-CH_3–C_3H_4) were prepared by the Wilke method [3].

Dichlorobutenes (DCBs) were 3,4-dichlorobutene-1 (3,4-DCB-1) and *cis*- and *trans*-1,4-dichlorobutenes-2 (1,4-DCB-2). DCBs were prepared by the liquid-phase partial chlorination of butadiene-1,3 in $CHCl_3$ at –20°C in the presence of $FeCl_3$. The mixtures of products of the butadiene-1,3 chlorination were separated by distillation (a column of 26 theoretical plates). DCBs used have the following purity characteristics: 1,4-DCB-2, at least 98% (a mixture of *cis*- and *trans*-isomers), at least 80% of individual isomers; 3,4-DCB-1, at least 98%.

Based on previous findings [2], we studied the reaction of nickel bis-η^3-allyl complexes $Ni(all)_2$ with dichlorobutenes under the following optimal conditions: the concentration ratio for $Niall_2$/DCB was 0.8–1.2 mol/mol; diethyl ether was a solvent; and the temperature was 10–30°C.

Experiments were carried out in a batch reactor (volume, 25 cm³) equipped with a sampler. A solvent and DCB were loaded into the reactor, oxygen was removed from the solution, and a weighed sample of the complex was transferred at a pressure of 0.1 Pa and a temperature of –196°C by the vacuum condensation method. The reactor was then allowed to heat to the reaction temperature, which was kept constant along with vigorous stirring.

Samples were analyzed and the reaction was monitored by gas chromatography (a Chrom 5 chromatograph, an 30 m × 200 μm SPB-20 capillary column, and the films were 0.25 μm thick).

Upon reaction completion, the products, solvent, and unreacted DCB were distilled off in a high vacuum. The distilled solution was examined by chromatography coupled with mass spectrometry (an MS-80 Kratos mass spectrometer attached to a Carlo-Erba 4200 chromatograph; mass spectra were recorded under electron impact mode at an ionization energy of 50 eV, an ionization current of 100 mA, and the source temperature was 150°C) and FTIR spectroscopy (a Bruker IFS-111V spectrometer coupled with a Carlo-Erba 4200 chromatograph, an SPB-1 capillary column, 30 m × 750 μm, a film thickness of 1 μm).

RESULTS AND DISCUSSION

Figure 1 shows typical kinetic curves, which characterize the changes in concentrations of the reactants and products during the reaction of $Ni(C_3H_5)_2$ with 1,4-DCB-2

at different temperatures. The reaction of $Ni(C_3H_5)_2$ with 3,4-DCB-1 is similar. Four stages of these processes can easily be distinguished.

At stage I, DCB is rapidly consumed, and hexadiene-1,5, 7-chloroheptadiene-1,5 (in the case of excess 1,4-DCB-2) and 3-chloromethylhexadiene-1,5 (in the case of excess 3,4-DCB-1) are formed. The concentrations of these compounds stop changing by the end of this stage.

Stage II is characterized by the formation of decatriene isomers at an almost unchanged concentration of free DCB.

No substantial change in the composition of the reaction mixture is observed at stage III of the reaction. DCB is not consumed, the formation of decatrienes almost ceases, and new products are not formed. This stage lasts 0.5–2 h depending on the temperature.

The main feature of stage IV is the formation of products of unusual allyl coupling, nonadienes and nonatrienes, as well as propene and hydrogen (traces). The concentrations of other organic components of the reaction system at this stage remain unchanged.

Even cursory analysis of the kinetic curves in Fig. 1 indicates that the interaction of $bis-\eta^3$-allylnickel and DCB is complex and that various reactions occur. The temporal separation of stages, which is a rare phenomenon in organometallic chemistry, is notable. This fact enables a more detailed study of reactions occurring at each stage.

The beginning of stage I is accompanied by a change in the color of the reaction solution. During mixing, the yellow color, which is due to $bis-\eta^3$-allylnickel, changes to dark red, which is more characteristic of nickel η^2-olefin complexes. The data of material balance indicate that ~80% of starting DCB is consumed at this stage; however, at most 10% of C_4H_6 fragments were observed in organic compounds formed ($C_7H_{11}Cl$ and $C_{10}H_{16}$).

Hexadiene-1,5 is the main and sometimes the only product of this stage. It follows from the kinetic data that the initial rate of its formation is described by the second-order equation: the first order with respect to $Ni(C_3H_5)_2$ and DCB,

$$\frac{dC_{C_6H_{10}}}{dt} = k_{app}C_{Ni(C_3H_5)_2}C_{DCB}.$$

Similar kinetic curves were obtained for the rate of DBC consumption, although the latter is much higher. Figure 2 shows the experimental values of the observed rate constants for different temperatures. They are satisfactorily described by the Arrhenius plots $\ln k_{app}-1/T$. The activation energies for C_6H_{10} formation (58 ± 3 kJ/mol for 1,4-DCB-2 and 62 ± 3 kJ/mol for 3,4-DCB-1) agree with similar values for other reactions of $bis-\eta^3$-allylnickel decomposition [4].

The behavior of the reaction system for cis- and trans-isomers of 1,4-DCB-2 is similar.
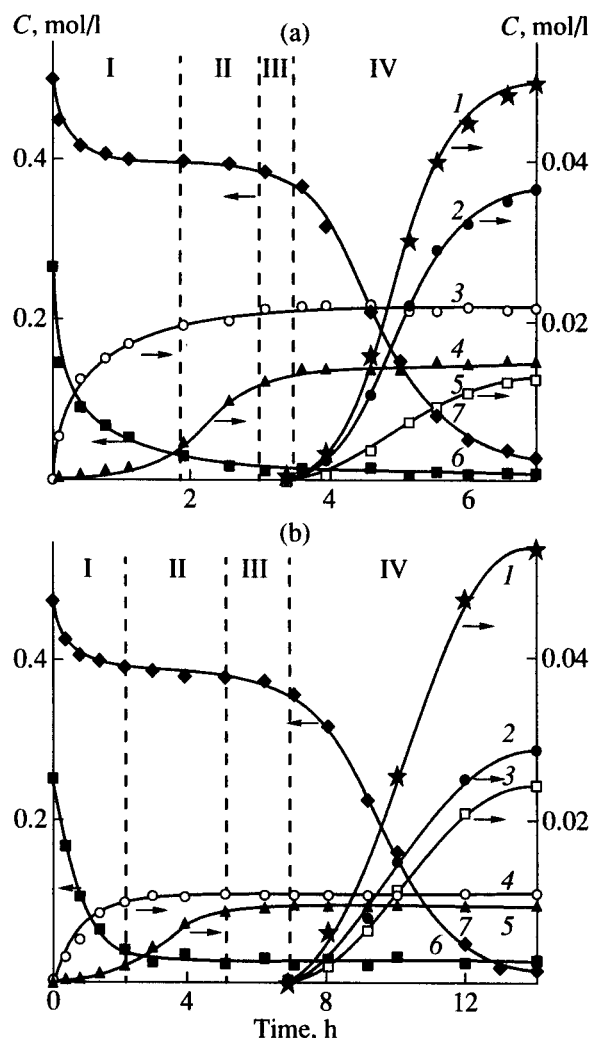
Fig. 1. Concentrations of reactants and products in the reaction of $bis-\eta^3$-allylnickel with 1,4-dichlorobutene-2 at (a) 30 and (b) 12°C: (1) sum of nonatrienes C_9H_{14}; (2) propene; (3) hexadiene-1,5 C_6H_{10}; (4) sum of decatriene $C_{10}H_{16}$; (5) sum of nonadienes C_9H_{16}; (6) 1,4-DCB; and (7) overall amount of allyl fragments calculated as the difference between their contents in starting $Ni(C_3H_5)_2$ and products. The boundaries of the stages (see text) are marked by dotted lines.

Almost the same set of products with similar ratios is formed in the case 1,4-DCB-2 and 3,4-DCB-1. Slight differences are related to the duration of stages I and II of the reaction and the formation of insignificant amounts of $C_7H_{12}Cl$ isomers (for excess DCB). Figure 2 shows that the observed rate constants of hexadiene-1,5 formation for 3,4-DCB-1 are several times lower than those for 1,4-DCB-2.

Based on the information obtained for stage I of the reaction, we may suggest some features of its mechanism, characterized by the following key steps (Scheme 1):

(1) The η^2-coordination of DCB at the nickel atom accompanied by the $\eta^3 \longrightarrow \eta^1$-isomerization of the first
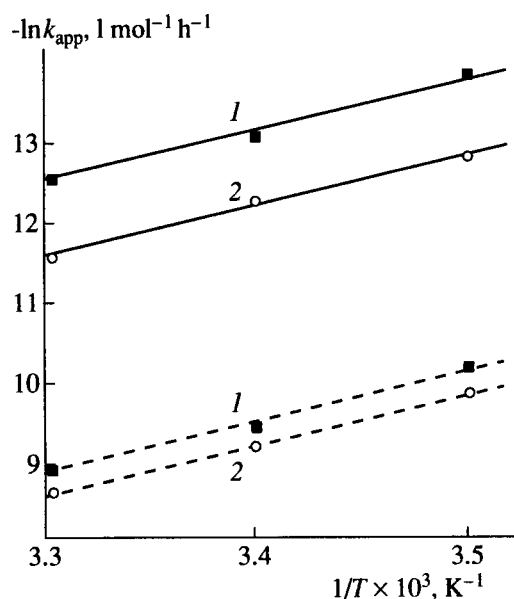
-lnk_{app}, l mol^{-1} h^{-1}

Fig. 2. The Arrhenius plot of k_{app} for the formation of hexadiene-1,5 (solid line) and consumption of DCB (dotted line) in the reactions (*1*) Ni(C$_3$H$_5$)$_2$ + 1,4-DCB-2 and (*2*) Ni(C$_3$H$_5$)$_2$ + 3,4-DCB-2.

(complexes **1.1a** and **1.1b**) and then the second allyl ligand (complexes **1.2a** and **1.2b**).

(2) The oxidative addition of the C–Cl bond of coordinated DCB to the nickel atom. Evidently, the chlorine atom of the allyl group participates in this step. Stage I is faster in the case of 1,4-DCB-2, which is explained by the fact that this compound has two chlorine atoms in the β-position relatively to the double bond, whereas 3,4-DCB-1 has only one, which is sterically less accessible.

(3) The reductive elimination of some allyl fragments and their substitution from the coordination sphere of the metal. The C$_4$H$_6$Cl fragment evidently more strongly binds to the nickel atom due to the electron-donor influence of the chlorine atom. Therefore, complexes **1.2a** and **1.2b** decompose to form mainly hexadiene-1,5. 7-Chloroheptadiene-1,5 is formed in a smaller amount.

Although stage I produces at most 20% of the overall amount of organic products of the reaction, the information on its regularities is important for the understanding of subsequent steps.

The balance experiments showed ~30% of allyl fragments that initially belonged to bis-η^3-allylnickel in the composition of organic products of stages I and II.

The concentration profiles for decatrienes formed at stage II are *S*-shaped, and they reach a steady-state level by the end of this stage. It can be assumed that intermediates responsible for decatriene formation are formed in steps of stage I.

The structure of decatrienes was determined by mass spectrometry coupled with chromatography and

FTIR spectroscopy coupled with chromatography. Two main products (*trans*-decatriene-1,5,9 and *trans*-decatriene-1,4,8) are linear. The fraction of other decatrienes is within 5% of all C$_{10}$H$_{16}$ molecules. According to our data, they are also linear *trans*-isomers. It is important that the same set of products with close ratios is formed from both DCB isomers. In the case of 1,4-DCB-2, the formation of linear decatrienes seems reasonable; in the case of 3,4-DCB-1, the presence of such compounds confirms the oxidative addition of this molecule involving the chlorine atom of the allyl group. The oxidative addition leads to the formation of 4-chloro-η^3-crotylnickel (intermediate **1.3**). The complex with a similar structure is also formed in the case of 1,4-DCB-2. Its further transformation can occur via two pathways (Scheme 2):

(1) The recombination of the C$_4$H$_6$Cl and C$_3$H$_5$ ligands to form coordinated 7-chloroheptadiene-1,5 (complex **2.1**), which in the case of excess DCB, can either be substituted from the complex or undergo secondary oxidative addition to the nickel atom to form decatrienes.

(2) The oxidative addition to the adjacent nickel complex. The C$_4$H$_6$ fragment formed in this reaction becomes a bridge between two nickel atoms. Taking into account that only ~10% DCB further transforms into decatrienes, we may assume that most C$_4$H$_6$ fragments remain in the composition of nickel complexes.

The secondary intramolecular oxidative addition of the 4-chlorocrotyl fragment to the nickel atom to form a butadienediallyl derivative (**2.2**) is doubtful because of energy and steric hindrances. Its counter-synthesis (Ni(C$_3$H$_5$)$_2$ + butadiene-1,3, Ni(C$_3$H$_5$)$_2$ + 4-chlorobutene-1, [(C$_3$H$_5$)NiCl]$_2$ + butadiene-1,4) and subsequent transformations lead to the formation of hexadiene-1,5 and oligomers of butadiene-1,3. Decatrienes, nonadienes, and nonatrienes were not found in these systems.

The formation of polynuclear nickel complexes is the essence of stages II and III. This process is intramolecular, the formation of decatrienes virtually ceases by the end of stage III, and oligomeric intermediates containing three and more nickel atoms are likely formed.

We isolated these complexes at different steps of stage III. For this purpose, all volatile components of the reaction were removed from the reaction solution by vacuum distillation. Volatile nickel compounds (Ni(C$_3$H$_5$)$_2$) were not found in the condensate. A light red glassy complex that remained on the reactor walls was subjected to elemental analysis on an S-800 Hitachi instrument with a Link Analytical attachment for analysis. The complex was taken from the reactor, put into a spectrometer chamber, and analyzed in the complete absence of oxygen.

The results of elemental analysis of the complexes are presented in the table. They show that the molecular composition of complexes generally remains unchanged during stage III.

Probable mechanism of stage I of the reaction of bis-η^3-allylnickel with dichlorobutenes
(A is 1,4-DCB-2, B is 3,4-DCB-1)

Scheme 1.
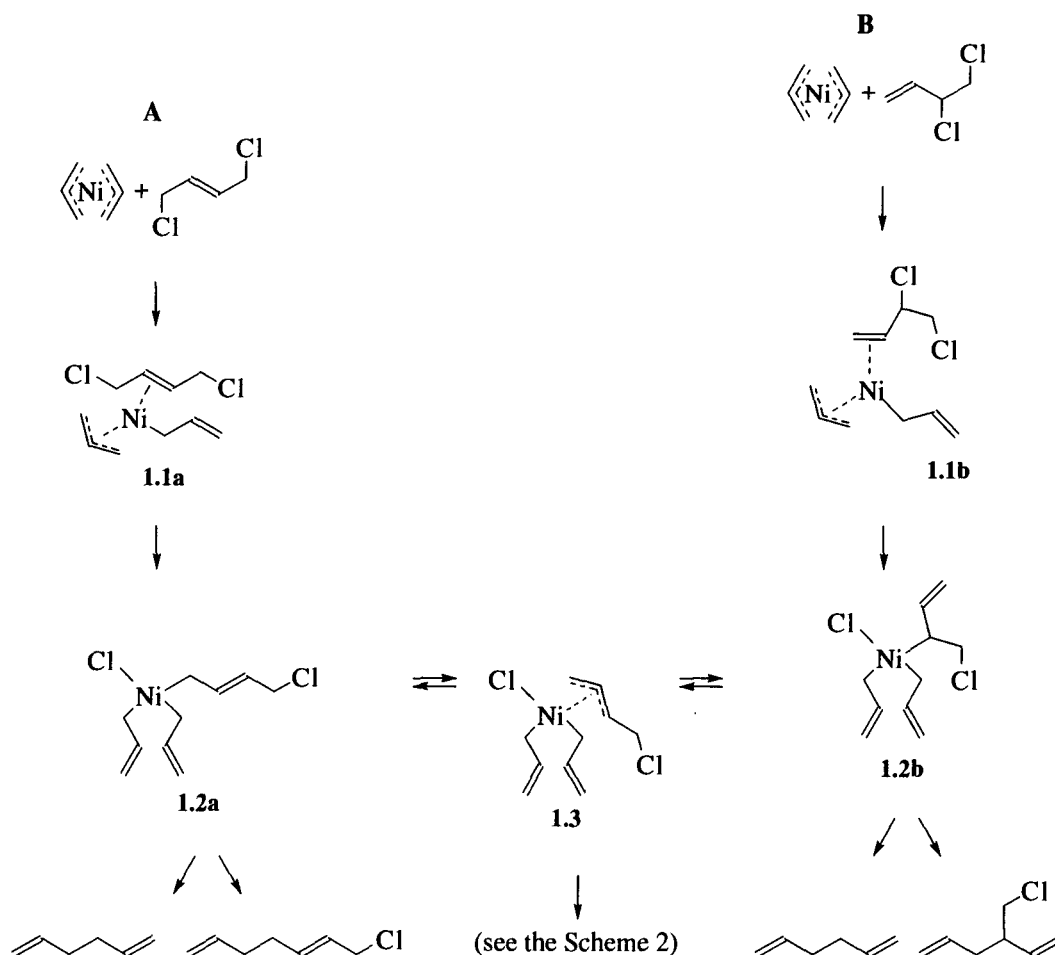
The elemental analysis data are in excellent agreement with the results of balance experiments, which make it possible to estimate the average amount of the starting fragments that entered the composition of intermediates. The relative amount of C_4H_6 decreased by 2–4%, and that of allyl fragments decreased by 4–8% due to the formation of $C_{10}H_{16}$. The concentrations of all components controlled by GLC also remained almost unchanged. Nevertheless, qualitative restructuring and aggregation of intermediates take place. We noticed a decrease in the color intensity of the reaction solution. Taking into account the experimental error (up to 5%) and reducing the number of fragments to the lowest integer, we may assume that the complex has the composition $Ni_4(C_3H_5)_6(C_4H_6)_3Cl_7$ at the end of stage III. In these complexes, C_4H_6 fragments most likely bridge nickel atoms. In fact, stage III is the induction period before the unusual coupling of the allyl fragments.

Compounds with molecular formulas C_9H_{14}, C_9H_{16} and propene are formed at stage IV of the reaction. Traces of molecular hydrogen were also found. C_9H_{14},

C_9H_{16}, and C_3H_6 are synchronously accumulated. At any time, the total molar concentration of C_9H_{14} isomers satisfactorily corresponds to the sum of C_9H_{16} isomers and propene.

The shapes of kinetic curves suggest that these compounds are formed via coupled pathways. The groups of compounds with the compositions C_9H_{14} and C_9H_{16}, C_9H_{14}, and C_3H_6 may have common intermediates in the final step of the process. If we assume intramolecular allyl coupling, which agrees with numerous published data [5–7], the intermediate producing C_9H_{14} and C_3H_6 should contain at least four allyl fragments. At least six of them are required for the simultaneous formation of C_9H_{14} and C_9H_{16}. This number of ligands cannot be coordinated to a mononuclear nickel complex. At stages II and III, the formation of polynuclear complexes is highly probable in which the spatial arrangement of allyl fragments favors their trimerization. The composition of the isolated intermediate does not contradict these concepts.

Probable mechanism of the formation of polynuclear nickel complexes
at stages II and III of the reaction
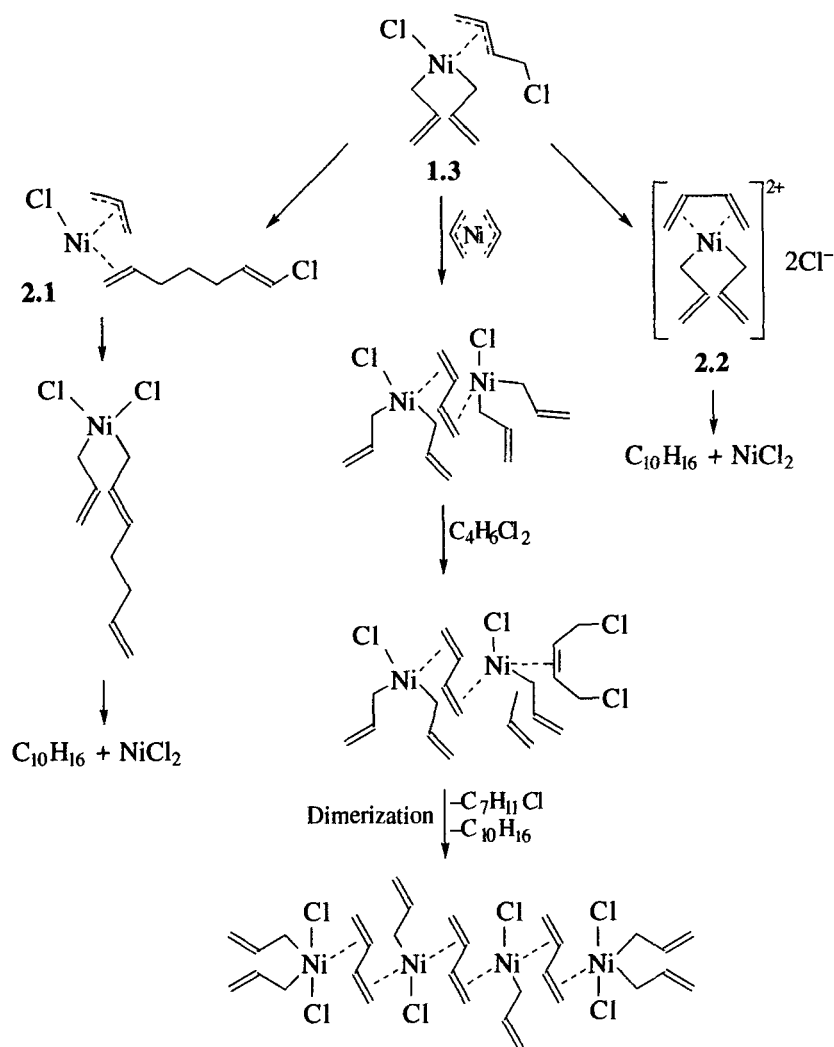
Scheme 2.

The formation of the nickel hydride intermediates in these complexes most likely becomes energetically favorable. Although these intermediates were not detected during the reaction, their existence is evident from the presence of molecular hydrogen in the system. This is also indicated by the composition of products of

oxidative (C_9H_{14}) and reductive (C_9H_{16}, C_3H_6) coupling formed from the C_3H_5 fragments. Hydride transfer between allyl fragments usually occurs through nickel hydride complexes [8].

In general, the temperature effect on the regularities of the process is nonuniform. For example, at stage I at

Results of elemental analysis and composition of complexes isolated at different stages of the reaction

Stage	Elemental analysis								Balance experiments							
	composition of complex, wt %				ratio of elements, mol/mol				fragment composition of elements, mol/mol				ratio of elements, mol/mol			
	Ni	C	H	Cl	Ni	C	H	Cl	Ni	C_3H_5	C_4H_6	Cl	Ni	C	H	Cl
Stage III, beginning	24.48	43.78	5.84	25.90	1.00	8.77	16.04	1.71	1.00	1.75	0.88	1.75	1.00	8.74	16.01	1.74
Stage III, end	26.34	40.39	5.39	27.88	1.00	7.52	12.06	1.73	1.00	1.50	0.75	1.75	1.00	7.49	12.03	1.75

30°C, more than 20% of hexadiene-1,5 is formed, whereas at 10°C, only 12% is formed; that is, the rate of stage I is much higher at higher temperatures.

The yield of decatrienes at stage II only slightly depends on temperature; the duration of stages II and III is shortened with an increase in temperature.

An increase in the temperature substantially accelerates stage IV. In addition, the ratio between the reduction products, C_9H_{16} and C_3H_6, also depends on this parameter. A higher temperature favors an increase in the relative amount of propene due to nonadienes. For example, at 30°C, the molar concentration of propene is 2.5–3 times higher than the concentration of nonadienes. By contrast, at 10°C, these compounds are formed in approximately equal amounts.

We studied the reactions of 1,4-DCB-2 with the closest analogs of bis-η^3-allylnickel, $Ni(1-CH_3C_3H_4)_2$, and $Ni(2-CH_3C_3H_4)_2$, to probe whether the reaction of unusual allyl coupling is general or not.

When bis-2-methyl-η^3-allylnickel was used, isomers of $C_{12}H_{20}$ (78%) formed due to the insertion of the C_4H_6 fragment between recombining 2-methylallyl ligands are the main products. We proved that the process occurred via this direction using deuterated 1,4-DCB-2. The product of recombination of the 2-methylallyl fragments, C_8H_{14} (6%), and $C_8H_{13}Cl$ isomers (10%) were also found. The products of unusual allyl coupling were not found.

By contrast, the products of usual allyl coupling (61%) dominate in the case of bis-η^3-crotylnickel. The insertion of the C_4H_6 fragment between recombining crotyl fragments occurs to a degree of 6%, and $C_8H_{13}Cl$ is formed with 8% yield. Compounds with molecular formulas $C_{12}H_{20}$ and $C_{12}H_{22}$ and a mixture of butenes were found for $Ni(1-CH_3C_3H_4)_2$. These compounds may be assumed to be the products of unusual allyl coupling of crotyl ligands. Their overall yield reaches 14%.

ACKNOWLEDGMENTS

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