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Norbornadienes in the Synthesis of Polycyclic Strained Hydrocarbons with Participation of Metal Complex Catalysts

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The advances achieved in recent years in the synthesis of polycyclic hydrocarbons, including those containing functional substituents, from norbornadiene and its derivatives using metal complex catalysts are surveyed. The homo- and codimerisation reactions of norbornadienes with olefins, dienes, and acetylenes, involving the $[2_\pi + 2_\pi]$-, $[2_\pi + 2_\pi + 2_\pi]$-, and $[4_\pi + 4_\pi]$-addition under the influence of transition metal complexes are examined. Data on the synthesis of norbornadiene trimers as well as the physicochemical and spectroscopic characteristics of a whole series of unique hydrocarbons are presented. The mechanisms of the reactions indicated are discussed.
The bibliography includes 173 references.

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INTRODUCTION

Since the publication of Schauzer' review,[1] devoted to the problems of the synthesis of strained skeletal hydrocarbons from bicyclo[2.2.1]hepta-2,5-diene [norbornandiene (NBD)] (I) by methods involving metal complex catalysis more than ten years have elapsed. During this period, particularly in recent years, this field of chemistry has continued to develop vigorously. As a result, extensive theoretical and experimental data have accumulated, being concentrated mainly in publications and patents which are not readily accessible to many chemists. Even superficial analysis of the latest data on the synthesis of skeletal compounds indicates increasing importance of NBD as the key and fundamental monomer for the synthesis in a single stage of unique polycyclic strained hydrocarbons, among which NBD homodimers, trimers, and codimers are of greatest interest and practical value. The hydrogenated NBD dimers are widely used in the USA for the synthesis of high-density and high-energy multipurpose hydrocarbon rocket fuels.[2]

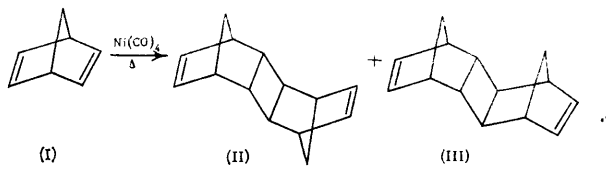
The transformations of norbornadienes into the corresponding cyclic dimers and trimers proceed as a rule under the influence of low-charge nickel, cobalt, iron, and rhodium complexes; manganese, chromium, titanium, palladium, and iridium compounds are used to a lesser extent. Active catalysts are obtained by reducing complexes of the above metals, soluble in organic solvents, with AlR_3, MgRR', and their derivatives. Transition metal complexes containing electron-donating or electron-accepting ligands in their coordination spheres are used in many instances.

The literature data are described systematically in the present review on the basis of the nature of the central metal atom, since in the majority of cases the direction and structural selectivity of cyclo-oligomerisation of norbornadienes are determined by precisely this factor.

II. THE HOMODIMERISATION OF NORBORNADIENE UNDER THE INFLUENCE OF METAL COMPLEX CATALYSTS

1. Catalytic Systems Based on Nickel Compounds

The cyclodimerisation of NBD via the $[2_\pi + 2_\pi]$addition mechanism was achieved for the first time by Bird et al.[3] using nickel tetracarbonyl as the catalyst. It was established subsequently[4-6] that $Ni(CO)_4$ promotes the formation of a mixture of isomers consisting of *endo,trans,endo*-pentacyclo[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]tetradeca-5,11-diene (II) and the *endo,trans,exo*-isomer (III) whose overall yield and composit on depend significantly on the dimerisation conditions.

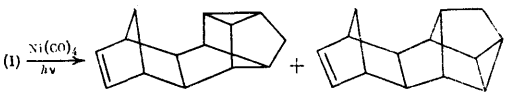


(I) (II) (III)

For example, when a mixture of NBD and $Ni(CO)_4$ with the ratio $Ni(CO)_4$: NBD = 1 : 100 is refluxed for 6.5 h, a mixture of the isomers (II) and (III) is obtained in a quantitative yield in proportions of 1 : 3.[5] When the reaction is carried out in benzene, the content of the dimer (III) increases markedly to give (II) : (III) = 1 : 5.[6]

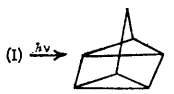
Complexes of unknown composition and structure, obtained when one of the three NBD $[2_\pi + 2_\pi]$dimers, namely *exo,trans,exo*-pentacyclo[8.2.1^{4,7}.0^{2,9}.0^{3,8}]tetradeca-5,11-diene (IV) or NBD itself is treated with nickel tetracarbonyl, drive the NBD cyclodimerisation reaction exclusively towards the formation of the isomer (III).[5] The yield of compound (III) varies from 69 to 91% depending on the conditions used in preparation of the complexes indicated.

The direction of the $[2_\pi + 2_\pi]$reaction changes when the NBD cyclodimerisation is carried out in the presence of catalytic amounts of $Ni(CO)_4$ with simultaneous UV irradiation. The $[2_\pi + 2_\pi + 2_\pi]$dimers (V) and (VI) are formed exclusively in these experiments in an overall yield of ~11%: [5]



(V) (VI)

Unfortunately, the authors[5] hardly discussed the mechanism of this interesting reaction. Under the conditions of UV irradiation, quadricyclane (QC) is probably formed initially and readily dimerises to the cyclic dimers (V) and (VI) under the influence of low-charge nickel carbonyl complexes containing in the coordination sphere NBD molecules together with carbon monoxide:



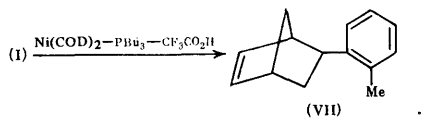
QC

This mechanisms has been confirmed by the results of studies[7-9] according to which quadricyclane is converted into $[2_\pi + 2_\pi + 2_\pi]$dimers and codimers in fairly high yields in the presence of complex catalysts based on nickel, palladium, and rhodium compounds.

The replacement of $Ni(CO)_4$ by $Ni(CO)_2(PPh_3)_2$ in the photoinitiated NBD cyclodimerisation reaction leads to the formation of the *exo,trans,exo*-isomer (IV) with a high selectivity.[10]

Cyclisation of the $[2_\pi + 2_\pi]$ type remains the principal pathways in the NBD dimerisation reaction using as catalysts zerovalent nickel complexes containing olefin, diene, and organophosphorus ligands in the coordination sphere. For example, $Ni(COD)_2$ (where COD = cyclo-octa-1,5-diene) converts NBD into the *exo,trans,exo*-dimer (IV) with a selectivity of 96.5%.[11] When triphenylphosphine is introduced into the composition of $Ni(COD)_2$, the selectivity in the formation of the dimer (IV) falls to 66.1% owing to the increase of the fraction of the *endo,trans,exo*-isomer (III).[12]

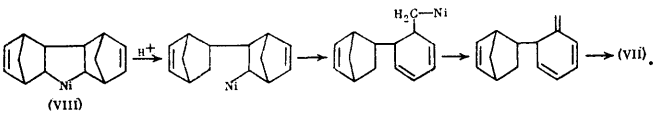
The dimerisation of NBD proceeds quite differently in the presence of the $Ni(COD)_2$–PBu_3 catalytic system promoted by CF_3CO_2H;[12] the only reaction product is then 5-exo-(*o*-tolyl)norborn-2-ene (VII), whose yield is 30%:



(VII)

Without the addition of trifluoroacetic acid, a mixture of NBD $[2_\pi + 2_\pi]$dimers (II)–(IV) was obtained in a yield of 60%, but the isomeric composition was not investigated.[12]

An analogous conversion of NBD into compound (VII) takes place in the presence of complexes of the type $NiX_2.PBu_3$ in solution in isopropylamine.[13] The introduction of $NaBH_4$ into the nickel–phosphine complex makes it possible to increase the yield of the product (VII) to 81.5%.[13] According to the authors,[13] the reaction proceeds via a mechanism whose first stage involves the activation of NBD via coordination with the central metal atom in the formation of the metallocyclic compound (VIII). In the presence of CF_3COOH, the latter undergoes a series of consecutive reactions leading to the formation of the dimer (VII):



(VIII)

Acrylonitrile complexes, which have been studied in detail by Schrauzer and Eichler[14] and which catalyse the dimerisation of NBD predominantly to the *endo,trans,exo*-isomer (III), play an important role in the series of nickel-containing catalysts of the dimerisation of NBD via the $[2_\pi + 2_\pi]$ addition mechanism.

The introduction of phosphines into acrylonitrile complexes of nickel increases the overall yield of dimers, which consist as a rule of the isomers (III) and (IV), to 80%, the selectivity in the formation of the isomer (III) being 98%.[14,15] It has been established that the ratio of the concentrations of the dimers (III) and (IV) is correlated with the electron density at the nickel atom: with increase of the effective charge on the central metal atom, the fraction of the isomer (III) also rises. Unfortunately, these data are insufficient to establish the detailed mechanism of the NBD cyclodimerisation reaction.

Thus the cyclodimerisation of NBD under the influence of nitrile complexes of nickel proceeds with the preferential formation of the *endo,trans,exo*-isomer (III) regardless of the nature and structure of the organophosphorus activator-ligands. With increase of reaction temperature, the fraction of this product in the reaction mixture increases.

Catalytic systems based on $Ni(CN)_2$ and phosphinites, phosphonites or phosphites are active in the cyclodimerisation of NBD also in the absence of a reducing agent.[16,17] For example, the catalyst prepared from $Ni(CN)_2$ and $PPh_2(OBu)$ converts NBD into a mixture of three possible $[2_\pi + 2_\pi]$ isomers (II)–(IV) in proportions of 62 : 5 : 33 and an overall yield of ~90%.

Under the reaction conditions, catalytically active nickel complexes are apparently formed on reduction of Ni^{2+} ions by the initial diene or the dimerisation products to Ni^+ or Ni^0. For example, in the presence of the complex $[Ni(acac)_2.(IV)]$, NBD is converted into the dimer (IV) in an overall yield of 53%.[4]

It is noteworthy that two- and three-component catalytic systems prepared from $Ni(acac)_2$, $AlEt_3$, and PPh_3, are much more productive than other known nickel-containing catalysts whose efficiency does not exceed 50–100 moles of the required product per gramme-atom of nickel.[4,11,18-23] Furthermore, the catalysts indicated are active in the dimerisation of NBD over a wide temperature range (20–200 °C) and effect the reaction both in the presence of solvents and in their absence. The yield of the mixture of dimers (II)–(IV) then varies from 40 to 87%. There is no doubt that these catalysts are extremely promising for the industrial application of the process.

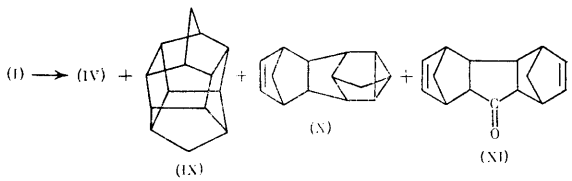
The foregoing permits the conclusion that nickel-containing complex catalysts catalyse the cyclodimerisation of NBD via the $[2_\pi + 2_\pi]$ mechanism with formation of pentacyclic hydrocarbons regardless of the nature of the anion attached to the metal atom and also of the structure of the ligands and the reaction conditions.

2. Iron-containing Catalysts in Norbornadiene Dimerisation Processes

Iron-containing catalysts, which are frequently used in NBD dimerisation processes, are characterised, in contrast to the nickel catalyst, by a wider spectrum of their activity. Depending on the nature of the selective complex (ligand

environment, oxidation state of iron) and the reaction conditions, they successfully effect all three variants of the NBD cyclodimerisation via the $[2_\pi + 2_\pi]$-, $[2_\pi + 2_\pi + 2_\pi]$-, and $[4_\pi + 4_\pi]$-addition mechanisms.

The formation of the NBD dimer in the presence of $Fe(CO)_5$ was first observed as early as 1959,[24] but the product obtained could not be identified. The above report[24] stimulated studies on the cyclodimerisation of NBD with participation of iron complexes. The complexes $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ were tested as catalysts of the dimerisation of NBD.[25–27] It was found that all the iron carbonyls exhibit catalytic activity in the NBD cyclo-oligodimerisation and lead to the formation of a complex mixture of hydrocarbons and carbonyl compounds. The dimers (IV), (IX), and (X) and the polycyclic ketones (XI), whose overall yields do not exceed 20%, were detected in the products.



(IX) (X) (XI)

The dimers (IV) and (IX) were identified as *exo,trans,exo*-pentacyclo[8.2.1.$1^{4,7}$.$0^{2,9}$.$0^{3,8}$]tetradeca-5,11-diene and heptacyclo[6.6.0.$0^{2,12}$.$0^{3,7}$.$0^{4,11}$.$0^{5,9}$.$0^{11,14}$]tetradecane, but final evidence for the correctness of these structures was obtained somewhat later.[28,29] The authors were unable to establish the structure of the hexacyclic dimers (X).

Iron nitrosyl complexes, distinguished by a high activity, productivity, and selectivity of their action, have been used[30] for the cyclodimerisation of NBD. The $[2_\pi + 2_\pi]$dimers (III) and (IV) were obtained exclusively in ~98% yield when $Fe(CO)_2(NO)_2$ was used.[30,31]

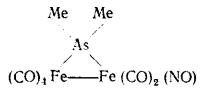
The study of Jolly et al.[30] initiated the systematic search for and development of highly active catalysts for the selective cyclo-oligomerisation of NBD. A whole series of iron nitrosyl complexes were obtained and investigated in the course of several years and certain characteristics of their action in NBD reactions were discovered.[32–43]

In particular, it was established that the catalytically active species responsible for the formation of the NBD dimer molecules was the coordination-unsaturated complex $Fe(NO)_2^*$,[30,31,39,40,42] which is probably formed under the reaction conditions when nitrosyl ferrates interact with NBD or its dimers.

Similar results were obtained in the electrochemical and chemical reduction of $[Fe(NO)_2Cl]_2$ in the presence of PPh_3.[39,40,42] The complex $[Fe(NO)_2Cl]_2$ is converted quantitatively into $Fe(NO)_2^*$ and the compounds $Na[Fe(CO)_3NO]$ and $Hg[Fe.(CO)_3NO]_2$ are converted into $Fe(CO)_2(NO)_2$, which the authors believe readily dissociates into CO and $Fe(NO)_2^*$.[44] Regardless of the structure and nature of the initial complex, only the $[2_\pi + 2_\pi]$dimers (III) and (IV) are formed in the presence of the systems indicated.

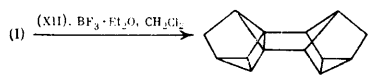
These results show that the mechanism of the cyclodimerisation of NBD under the influence of different iron nitrosyl complexes remains unchanged. The nature of the reductant hardly affects the yield of the dimers (III) and (IV) and the reaction selectivity. When powdered zinc is used as the reducing agent, the degree of conversion of NBD depends markedly on the nature of the solvent. Thus high yields of dimers (93%) have been obtained in acetone and tetrahydrofuran (THF). When the reaction is carried out in toluene, methanol, and acetonitrile, the yield of dimers falls.[38] In the presence of the $[Fe(NO)_2Cl]_2/AgBF_4$ catalytic system, best results are obtained in the dimerisation of NBD in pure methylene chloride. The selectivity in the formation of the dimer (IV) then amounts to 94% for a degree of conversion of NBD of 76%. It is noteworthy that $AgBF_4$ is the most effective promoting agent among the cocatalysts tested.

A high catalytic activity and selectivity in the reaction of the cluster compound (XII), which belongs to be class of iron carbonyl nitrosyl complexes considered, has been observed recently. At 60 °C in benzene, it converts NBD quantitatively into the *exo,trans,exo*-dimer (IV).[45,46]



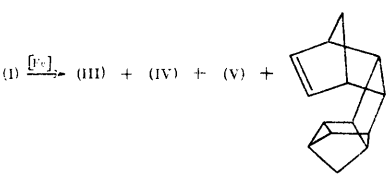
(XII)

A unique instance of a change in the selectivity in the dimerisation of NBD has been observed when an equimolar amount of $BF_3.OEt_2$ was added to compound (XII).[45] The only reaction product is the dimer (XIII), namely *endo,endo*-heptacyclo[8.4.0.0^{2,12}.0^{3,8}.0^{4,6}.0^{5,9}.0^{11,13}]tetradecane ("Binor-S"), formed via $[4_\pi + 4_\pi]$cycloaddition:



(XIII), (100%)

An author of several patents,[4,19,47] who used the $Fe(acac)_3$–$AlEt_3$ and $Et_2Al(OEt)$ catalytic systems for the dimerisation of NBD, achieved major successes in the synthesis of pentacyclic and hexacyclic NBD dimers. Iron acetylacetonate, reduced with triethylaluminium, catalyses the dimerisation of NBD with formation of a mixture of four hydrocarbons (III), (IV), (V), and (XIV):



(XIV)

The hexacyclic isomers (V) and (XIV) have been identified by Scharf et al.[48] The ratio of the isomers formed and the overall yield depend on the reaction conditions and the method of preparation of the catalyst. The addition of the olefin to the catalyst prepared at 0 °C and heating at 40 °C for 20 h result in the formation of a mixture of dimers of the following composition in a yield up to 97%: 63.6% (III), 24.3% (IV), and 12.1% [(V) + (XIV)].[4] The simultaneous addition of NBD solutions of $Fe(acac)_3$ and $AlEt_3$ to the reactor heated to 140–200 °C makes it possible to obtain mixtures of the isomers (III)–(V) and (XIV) containing 64–72% of hexacyclic hydrocarbons.[49–51]

The use of 1,2-bis(diphenylphosphino)ethane (BPE) and replacement of triethylaluminium by diethylaluminium chloride in the $Fe(acac)_3$–AlR_3 catalytic system make it possible to increase the selectivity in the formation of the *exo,exo-dimer* (VI) to 80–90%,[52,53] while the addition of triphenylphosphine alters the direction of the reaction towards the preferential formation of the *endo,endo*-isomer (XIV).[54]

Biscyclo-octatetraeneiron and the catalytic system obtained by reducing $FeCl_3$ with isopropylmagnesium chloride catalyse the dimerisation of NBD to the isomers (IV) and (VI) with the preferential formation of the latter.[55] When $FeCl_3$ is reduced with triethylaluminium or sodium, a catalyst active in the $[2_\pi + 2_\pi + 2_\pi]$cycloaddition is also obtained.[56]

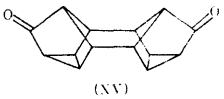
Thus, among the iron-containing NBD dimerisation catalysts investigated, the highest activity and productivity (up to 1000 moles of NBD converted per gramme-atom of iron) is shown by catalytic systems of the Ziegler–Natta type: $Fe(acac)_3$–$AlR_3(AlEt_3)$ or $Et_2Al(OEt)$. They are superior to the analogous nickel catalysts because of the consistently high yield of the dimers (70–90%) and the better reproducibility of the results.

3. Dimerisation of Norbornadiene in the Presence of Cobalt Catalysts

Cobalt compounds exhibit an exceptionally high catalytic activity in the cyclo-oligomerisation reactions of NBD. The first report of their use for the dimerisation of NBD dates back to 1961;[26] however, the above communication does not contain experimental details. In a classical study[28] devoted to the determination of the stereochemistry of the NBD $[2_\pi + 2_\pi]$ dimers, it was later shown that $Co_2(CO)_8$ combined with PPh_3 converts NBD into a mixture of two $[2_\pi + 2_\pi]$ isomers: the *endo,trans,exo*-isomer (III) and the *exo,trans,exo*-isomer (IV) with a (III) : (IV) ratio of 1 : 10.

Interesting results have been obtained in the dimerisation of NBD in the presence of the $Co(CO)_3(NO)$ catalyst isoelectronic with the complex $Fe(CO)_2(NO)_2$.[30] It was found that the former effects $[2_\pi + 2_\pi]$cycloaddition. In these experiments $[2_\pi + 2_\pi + 2_\pi]$dimers were formed together with compound (IV). The quantitative composition of the hexacyclic hydrocarbons (V) and (XIV) is not stated in the above communication. Furthermore, the dimer (IV) can be obtained with a selectivity up to 98% when the complex $[Co(NO)_2Cl]$ or $[Co(NO)_2Br]$, promoted with $AgPF_4$ or $NaBPh_4$, is used as the catalyst.[32,34–36]

In studies[1,57,58] of the catalytic properties of cobalt compounds in the cyclo-oligomerisation reactions of cyclic olefins and dienes, it has been observed that complexes of the type $M[Co(CO)_4]_n$ (where M = Zn, Cd, or Hg) effect the stereospecific dimerisation of NBD via the $[4_\pi + 4_\pi]$mechanism with formation of "Binor-S" (XIII) (in 95% yield). The structure of compound (XII) could not be demonstrated for a long time. However, the specific synthesis by the Wolff–Kishner reduction of the diketone (XV)[59,60] made it possible to establish finally that the dimer (XIII) has, as already suggested,[57,58] the structure of *endo,cis,endo*-heptacyclo[8.4.0.$0^{2,12}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$.$0^{11,13}$]tetradecane.

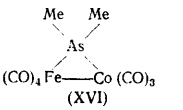

(XV)

$\longrightarrow$ (XIII).

In order to carry out the cyclodimerisation of NBD to compound (XIII) under the influence of the catalysts investigated, it is essential to have cocatalysts of the type BF_3, SbF_3, $AlBr_3$, and $BF_3.OR_2$, whose greatest efficiency is achieved when the ratio of $M[Co(CO)_4]n$ and the Lewis acid is 1 : 8. The introduction of Lewis bases (pyridine and triethylamine) into the catalysts promotes the preferential formation of pentacyclic and hexacyclic dimers.[57,61]

Dinuclear and polynuclear cobalt catalysts of the cyclodimerisation of NBD to the penta-, hexa-, and hepta-cyclic dimers (III), (IV), (V), (XIII), (XIV) were subsequently obtained and investigated. The activity and selectivity of the action of these catalysts depend greatly on the nature of the anion in the coordination sphere of the central metal atom and also on the structure of the cocatalyst (Lewis acid), the nature of the solvent, and the reaction conditions.[57,59,62–69] For example, the trinuclear complex (XVI) converts NBD into a 1 : 1 mixture of the dimers (XIV) and (XIII). When the Lewis acid $BF_3.OEt_2$ is introduced into the catalyst, the process can be directed towards the formation of compound (XIII) (in ~100% yield):[45,46]

$$(IV) \xleftarrow{(XVI)} (I) \xrightarrow{(XVI)+BF_3\cdot OEt_2} (XIII)$$


(XVI)

The study of the kinetics of the cyclodimerisation of NBD to "Binor-S" (XIII) in the presence of the dinuclear catalyst $(Ph_2C_2)Co(CO)_6$ established that the reaction is first order with respect to the catalyst and that the activation energy is ~38.58 kcal mol^{-1}.[63]

Systems obtained by reducing $Co(acac)_2$ with organoaluminium compounds have a high catalytic activity in the NBD dimerisation reactions. The dimers (III) (29%) and (IV) (62%) and the $[2_\pi + 2_\pi + 2_\pi]$dimers (X) (yield 9%) of unknown composition are formed in the presence of the $Co(acac)_2$–$AlEt_3$ system:[4]

$$(I) \longrightarrow \underset{29\%}{(III)} + \underset{62\%}{(IV)} + \underset{9\%}{(X)}$$

The authors note[53] that the direction of the NBD cyclodimerisation can be completely altered by employing the three-component $Co(acac)_2$–1,2-bis(diphenylphosphino)ethane–Et_2AlCl system as the catalyst. In this case the dimer (VI) is formed quantitatively. The replacement of the bisphosphine by PPh_3 leads to the formation of the isomer (XIII).[61]

Thus the cobalt-containing catalysts are extremely effective in the synthesis of the heptacyclic NBD dimer "Binor-S", which has found extensive applications in the synthesis of diamond-like structures.

4. Complexes Based on Rhodium in the Norbornadiene Dimerisation Processes

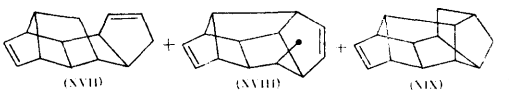
It is noteworthy that rhodium catalysts are distinguished by a low selectivity in the NBD dimerisation processes and as a rule lead to the formation of a complex mixture of polycyclic hydrocarbons. The fundamental studies on the application of rhodium-containing catalysts in the NBD dimerisation reactions have been carried out by Katz and co-workers (Columbia University). These investigators were able to isolate and identify a whole series of NBD dimers and trimers with the aid of modern physicochemical methods. Unfortunately, they investigated and tested only a limited number of rhodium complexes capable of effecting the dimerisation or trimerisation of NBD.

For example, the dimerisation of NBD in the presence of the 5% Rh/C catalyst takes place relatively selectively; NBD is then converted into a mixture of the isomers (IV), (V), and (XIV) in 53% yield:[71]

$$(I) \xrightarrow{Rh/C} \underset{4\%}{(IV)} + \underset{84\%}{(V)} + \underset{12\%}{(XIV)}$$

In the presence of Wilkinson's complex $[Rh(PPh_3)_3Cl]$, the dimerisation of NBD is accompanied by the skeletal isomerisation of the *exo,endo*-hexacyclo[9.2.1.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$]tetradec-12-ene (V) to the hydrocarbons (XVII), (XVIII), and (XIX):[29,72]

(I) $\longrightarrow$ (V) + (IX) +


(XVII) (XVIII) (XIX)

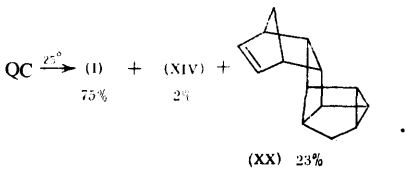
The introduction of an additional amount of PPh_3 into the complex $[Rh(PPh_3)_3Cl]$ hardly affects the direction of the dimerisation reaction,[29] but the composition of the cyclodimerisation products changes appreciably under these conditions.

The rhodium catalysts obtained by reducing $[Rh(PPh_3)_3Cl]$ with Et_2AlCl or $EtAlCl_2$ convert NBD into "Binor-S" (XIII) in an almost quantitative yield.[73] Analogous results have been obtained using catalytic systems with a fairly complex structure: $Rh(NBD)_2PF_6-PPh_3$, $P(OPh)_3$] or $[Rh_4(CO)_{12}-BF_3.OEt_2]$.[64,71] The dimerisation of NBD under the influence of complexes of the type of $Rh(NBD)_2BF_4$ results in the formation of mainly the hexacyclic dimers (V), (VI), and (XIV):[75]

$$(I) \xrightarrow{[Rh]} \underbrace{(V)+(VI)}_{60\%} + \underset{10\%}{(XIV)} .$$

A selective method of synthesis of the dimer (V) using rhodium catalysts has been proposed by Japanese workers.[13] The authors used the catalytic system $Rh(C_8H_{14})Cl-CF_3CO_2H$ (C_8H_{14} = cyclo-octene; Rh : CF_3COOH = 1 : 4).

It is noteworthy that, in contrast to other catalysts, the rhodium complexes are capable of converting quadricyclane (QC) into the corresponding NBD dimers. For example, when quadricyclane is treated with the carboxylate complex $[Rh(NBD)AcO]_2$ in methylene chloride at room temperature, NBD is mainly formed together with a small amount of the hexacyclic dimers (XIV) and (XX). The *endo,exo*-isomer (XX) has been obtained by a catalytic process only under the conditions indicated:[7]



It is believed[76] that the initial NBD plays the role of a reductant in relation to the rhodium(II) carboxylate complexes. According to these workers,[76] the NBD dimerisation process begins only after the conversion of rhodium(II) into rhodium(I) under the influence of NBD. The rhodium(I) complex formed under these conditions is an effective catalyst of the $[2_\pi + 2_\pi + 2_\pi]$cyclo-dimerisation of NBD. It has been noted[74] that the activity of the rhodium trifluoroacetate complexes is higher by an order of magnitude than that of the acetate complexes. Fairly active catalysts of the dimerisation of NBD to a mixture of compounds(V) and (XIV) have been obtained by reducing $Rh(acac)_3$ with the organoaluminium compounds Et_2AlCl and $EtAlCl_2$.[77]

The above studies exhaust the available literature data on the use of rhodium complexes in the cyclodimerisation reactions of NBD. It follows from the results presented above that catalysts based on rhodium salts and modified by Lewis bases or acids have universal properties and make it possible to obtain seven of the nine of the known NBD dimers. However, only a limited number of rhodium complexes have so far been investigated and tested as catalysts of the cyclo-oligomerisation of NBD and its derivatives can lead to the creation of new highly effective catalytic systems for the selective synthesis of polycyclic hydrocarbons with the unique structure from NBD and its derivatives.

5. Dimerisation of Norbornadiene in the Presence of Other Catalysts

Apart from the nickel-, iron-, cobalt-, and rhodium-containing catalysts, systems based on chromium, manganese, palladium, and iridium compounds as well as phenyl-lithium are used for the cyclodimerisation of NBD.[9,78,80,164]

In particular, the photolysis of chromium hexacarbonyl in solution in NBD leads to the formation of a mixture of pentacyclic hydrocarbons consisting of the *endo,trans,endo*-(II), *endo,trans,exo*-(III), and *exo,trans,exo*-(IV) isomers in

The physicochemical properties of the norbornadiene dimers.

Compound	B.p., °C/*p*, mmHg	M.p., °C	n_D^{20}	d_4^{20}	(M.p.)^h, °C	$(d_4^{20})^h$	Refs.
(II)	75/0.2	92—93	1.516*	—	99—102	—	[28, 84]
(III)	75/0.2	—25	—	—	38—39	—	[28, 84]
(IV)	237/760	67—68	1.518**	—	63.8±0.6	0.983***	[28, 84, 85]
(V)	117—119/10	14—16	1.5457	1.092	21.1±0.7	1.068****	[48, 85]
(VI)	—	—	—	—	12.3±0.2	1.077	[85]
(IX)	—	165—165.5	—	—	—	—	[25]
(XIII)	73/1—2	65—65.5	—	—	—	—	[57]
(XIV)	122/10	—23+—21	1.5521	1.105	8.0±0.2	1.089	[48, 85]
(XX)	121—122/10	—	1.5446	1.09	—	—	[48]

Notation: B.p.= boiling point; *p* = pressure, M.p. = melting point, d_4^{20} = density, n_D^{20} = refractive index, and (M.p.)^h and $(d_4^{20})^h$ are the values for the hydrogenated dimer.
*At 94 °C; **at 79 °C; ***at 70 °C; ****at 30 °C.

Note. Numbers in square brackets denote references (Ed. of Translation).

proportions of 1.4 : 1.0 : 1.8 respectively.[78] According to Carbonaro et al.,[79] manganese catalysts are active in the NBD cyclodimerisation reaction, but the authors do not present detailed data on the yield and composition of the dimers formed.

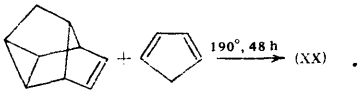
The possibility of using palladium complexes for the selected conversion of quadricyclane (QC) into a mixture of the dimers (V) and (VI) in a high yield have been demonstrated in a recent communication:[9]

$$QC \xrightarrow{Pd_2(DBA)_3(CHCl_3)} (V) + (VI);$$

DBA = PhCH=CH—CO—CH=CHPh .

Phenyl-lithium reacts with bicyclo[2.2.1]hepta-2,5-diene in ether and gives rise to a mixture of two NBD dimers whose yield depends on the ratio of the initial reactants.[80]

The NBD dimer (XX), which is difficult to synthesis, can be obtained in ~77% yield from deltacyclene (XXI) and cyclopentadiene by the Diels–Alder reaction:[48,81]



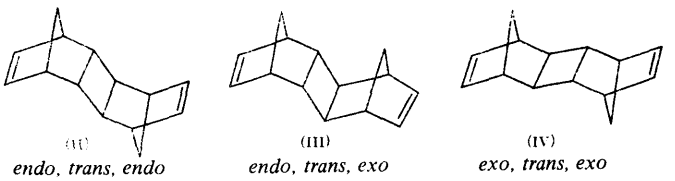
(XXI)

6. The Physicochemical Properties of Norbornadiene Dimers

Out of the fourteen theoretically possible NBD dimers, capable of being formed only as a result of bond cyclisation via reactions of the $[2_\pi + 2_\pi]$, $[2_\pi + 2_\pi + 2_\pi]$, and $[4_\pi + 4_\pi]$ types, nine have been actually synthesised. The physicochemical characteristics of these compounds as well as their hydrogenated derivatives are presented in the Table. The formation of other NBD dimers, namely (XVIII) and (XIX), which are the products of further reactions (skeletal rearrangement) of the hexacyclic isomers, has been noted in a series of studies.[29,72]

The theoretically possible NBD dimers are presented below.†

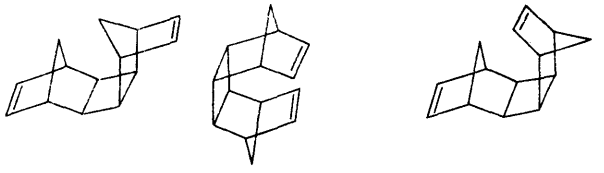
(1) Pentacyclic hydrocarbons: pentacyclo[8.2.1.$1^{4,7}$.$0^{2,9}$.$0^{3,8}$]deca-5,11-dienes—the products of the NBD $[2_\pi + 2_\pi]$dimerisation:



(II) *endo, trans, endo*

(III) *endo, trans, exo*

(IV) *exo, trans, exo*



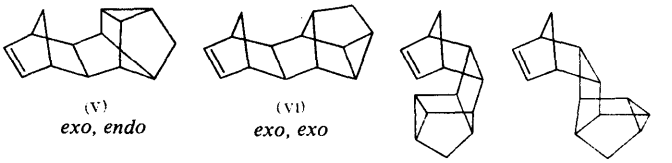
(XXII) *exo, cis, exo* (not obtained)

(XXIII) *endo, cis, endo* (not obtained)

(XXIV) *exo, cis, endo* (not obtained)

† The names of compounds (II)–(VI), (IX), (XIII), (XIV), (XX), and (XXII)–(XXVI) have been revised in accordance with new recommendations.[82,83]

(2) Hexacyclic hydrocarbons: hexacyclo[9.2.1.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$]tetradec-12-enes—the products of the NBD $[2_\pi + 2_\pi + 2_\pi]$dimerisation:



(V) *exo, endo*

(VI) *exo, exo*

(XIV) *endo, endo*

(XX) *endo, exo*

(3) Heptacyclic hydrocarbons—the products of the NBD $[4_\pi + 4_\pi]$dimerisation.

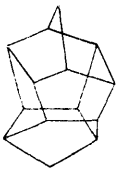
(a) Heptacyclo[8.4.0.$0^{2,12}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$.$0^{11,13}$]tetradecanes:



(XIII) *endo, cis, endo* ("Binor-S")

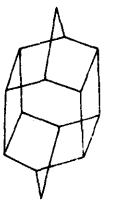
(XXV) *endo, trans, endo* (Binor-A obtained by the isomerisation of Binor-S)

(b) Heptacyclo[6.6.0.$0^{2,12}$.$0^{3,7}$.$0^{4,11}$.$0^{5,9}$.$0^{10,14}$]tetradecane:



(IX)

(c) Heptacyclo[9.3.0.$0^{2,5}$.$0^{5,13}$.$0^{4,8}$.$0^{6,10}$.$0^{9,12}$]tetradecane:



(XXVI) (not obtained)

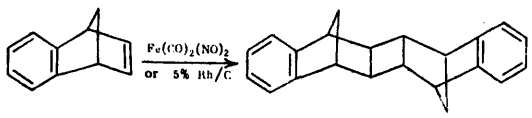
Owing to the complexity of their structures, the determination of the stereochemistry of the NBD dimers required much effort by investigators. In analysing the available data, one must note that the most convincing and unambiguous conclusions concerning the structure of polycyclic hydrocarbons can be obtained using the entire range of modern spectroscopic methods.[28,29] Studies of the ^{13}C NMR spectra of all the known NBD dimers and their hydrogenated derivatives are therefore of undoubted interest and practical value.[87]

III. THE HOMO- AND CO-DIMERISATION OF SUBSTITUTED NORBORNADIENES

The early studies on the catalytic reactions of substituted NBD includes those on the homocyclodimerisation of 1-, 2-, and 7-methylbicyclo[2.2.1]hepta-2,5-dienes under the influence of the complexes $Ni[P(OPh)_3]_4$ and $Fe(acac)_3$–$AlEt_3$.[20,21,49,51] The authors believe that mainly $[2_\pi + 2_\pi]$- and $[2_\pi + 2_\pi + 2_\pi]$-dimers are formed in these experiments, but the

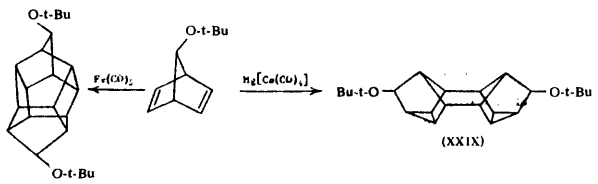
individual products were not isolated and identified. Unfortunately, the above communications do not contain data on the basis of which one could estimate and compare the activities of the substituted NBD in reactions catalysed by transition metal complexes.

Regardless of the nature of the catalyst [5% Rh/C or $Fe(CO)_2(NO_2)$], benzonorbornadiene is converted exclusively into compound (XXVII):[81,92]



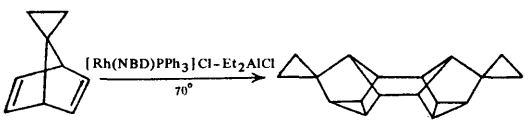
(XXVII), *exo, trans, exo*

According to Ennis et al.,[86] 7,14-dimethylheptacyclo-[8.4.0.$0^{2,12}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$.$0^{11,13}$]tetradecane is formed on dimerisation of 7-methylnorbornadiene under the influence of the catalyst $(NBD)_2Co_2(CO)_4$–BF_3.OEt_2.[85] It was established that the introduction of the fairly bulky t-butoxy-group in the 7-position, which is most remote from the double bond, does not have an appreciable influence on the stereospecificity of the dimerisation reaction. Depending on the nature of the catalyst, either 6,13-di-t-butoxyheptacyclo-[6.6.$0^{2,12}$.$0^{3,7}$.$0^{4,11}$.$0^{5,9}$.$0^{11,14}$]tetradecane (XXVIII) or the disubstituted "Binor-S" (XXIS) is formed:[60,88–90]



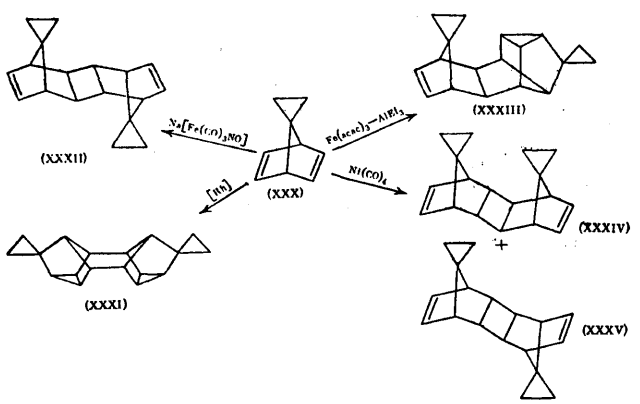
(XXIX)

The reactions of 7,7-disubstituted NBD, namely spiro-{bicyclo[2.2.1]hepta-2,5-diene-7,1^1-cyclopropane} (XXX), were investigated for the first time in fair detail in a number of studies.[91,92,94] The [4_π + 4_π]cyclodimerisation of compound (XXX), achieved recently with formation in a single stage of the nonacyclic compound (XXXI), is evidence for the exceptional effectiveness of the method involving metal complex catalysis in the synthesis of strained skeletal hydrocarbons.[91]

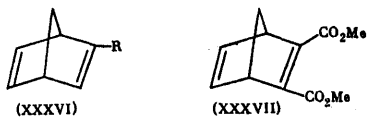


(XXX) (XXXI), 95%

It has been established[93–95] that the reactivity of compound (XXX) in cyclodimerisation reactions is not inferior to that of NBD, for which it has been possible to obtain the [2_π + 2_π]- and [2_π + 2_π + 2_π]dimers:



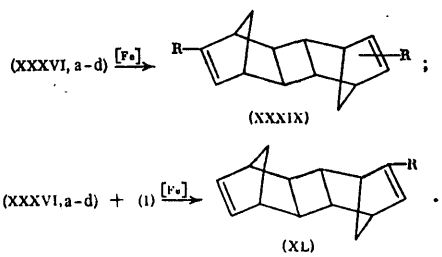
The results of the study of the catalytic homo- and co-dimerisation of 2- and 7-substituted NBD (XXVI, a–g), (XXX), and (XXXVII) in the presence of the complexes $Fe(CO)_2(NO_2)$ and $Na[Fe(CO)_3(NO)]$ were published for the first time by Dzemilev and co-workers:[93,95]



(XXXVI) (XXXVII)

R = Me(a), CH_2OH(b), CH_2OMe(c), CO_2Me(d), Cl(e), CHO(f), CH_2OAc(g)

It was found that only the dienes (XXXVI, a–d) and (XXX) are involved in the homodimerisation reaction and in codimerisation with NBD, the products being the 5(6),11-disubstituted and 5-monosubstituted *exo, trans, exo*-pentacyclo-[8.2.1.$1^{4,7}$.$0^{2,9}$.$0^{3,8}$]tetradeca-5,1-dienes (XXXIX) and (XI):

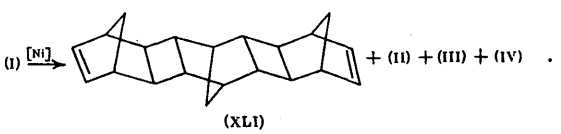


The selectivity in the formation of the *exo, trans, exo*-dimers is fairly high (≥91%).

The substituted NBD (XXXVI, e–g) do not form homodimers. The reduced reactivity of the dienes (XXXVI, e–g) may be caused by the change in the energy of the π orbitals as a function of the nature of the substituent. However, the results obtained in a study[95] of 2- and 7-substituted NBD by photoelectron spectroscopy permitted a quantitative demonstration that the energy of the π orbitals of the 1,4-diene system in substituted NBD varies only slightly. The authors[95] therefore assume that the low reactivity of compounds (XXXVI, e–g) can be accounted for by their involvement in the formation of coordination-saturated complexes with the central metal atoms, which are relatively inactive in homo- and co-dimerisation processes. This conclusion was confirmed by the fact that even smaller amounts of the above monomers added to the reaction medium deactivate the catalyst and suppress the dimerisation of both NBD and of the substituted NBD (XXXVI, a–d).

IV. THE SYNTHESIS OF NORBORNADIENE TRIMERS

Up to 1983, only two norbornadiene trimers had been obtained and isolated in low yields from a mixture of polycyclic products of the reaction of NBD under the influence of metal complex catalysts based on nickel and rhodium compounds.[4,9–11,18,29,71,72,75,76] For example, in the presence of $Ni(PPh_3)_4$, $Ni(CO)_2$, $(PPh_3)_2$, or Ni^0–PPh_3, NBD is converted into *exo, trans, exo, trans, exo*-octacyclo[8.8.1.1^{4,7}.1^{13,16}.$0^{2,9}$.$0^{3,8}$.$0^{11,18}$.$0^{12,17}$]heneicosa-5,14-diene (XLI) in ~5% yield:[4,10,11,18]

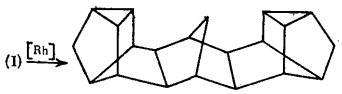


(XLI)

According to Ref.4, the yield of compound (XLI) increases to 40% when the cyclotrimerisation of NBD is carried out in dioxan in the presence of catalytic amounts of $Ni(COD)_2$. Unfortunately, subsequently none of the investigators, including the authors of the present review, were unable to reproduce these results.

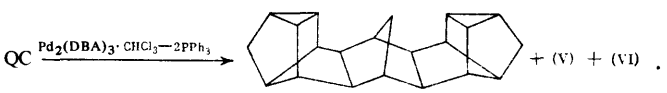
A more reliable method of synthesis of compound (XLI) consists apparently in the cyclocodimerisation of NBD with the *exo,trans,exo*-dimer (IV) in the presence of the $Ni(CO)_2 \cdot (PPh_3)_2$ catalyst.[10]

The saturated trimer (XLII) with two cyclopropane fragments has been obtained by the cyclotrimerisation of NBD with participation of the rhodium catalysts 5% Rh/C, $Rh(NBD)_2BF_4$, and $[Rh(CF_3CO_2)_2]_2$:[71,75,76]



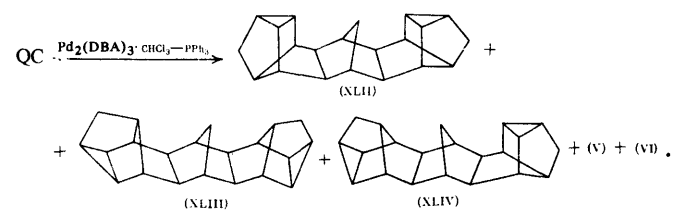
(XLII)

The synthesis of compound (XLII) under the influence of the dibenzylideneacetone (DBA) complex of palladium activated by triphenylphosphine has been reported recently:[9]



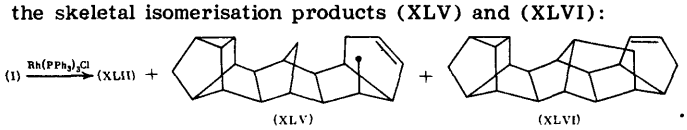
(XLII)

In a later publication[96] it was shown that Itoh's results required significant revision. It was found that the three isomeric cyclic trimers (XLII)–(XLIV) are formed together with the dimers (V) and (VI):



(XLII) (XLIII) (XLIV)

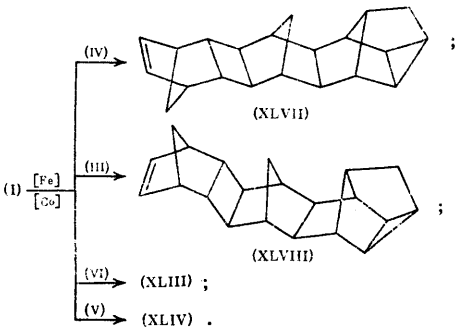
In addition, the trimer (XLII) was synthesised (in a low yield) by heating NBD with Wilkinson's complex $Rh(PPh_3)_3Cl$.[29,72] However, the preparative value of these studies is low, since the isolation of compound (XLII) in a pure form is very difficult owing to the presence in the reaction mass of the skeletal isomerisation products (XLV) and (XLVI):



(XLV) (XLVI)

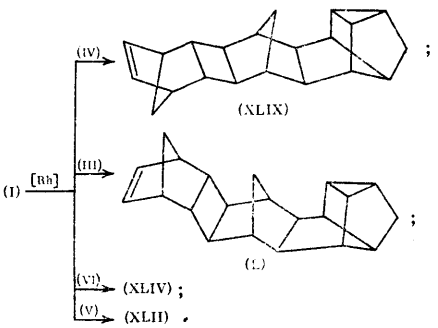
Effective methods have been developed[97] for the synthesis of the trimers (XLIII), (XLIV), (XLVII), and (XLVIII), which had not been described before, by the cyclodimerisation of NBD with the known dimers (III)–(VI) in the presence of the three-component catalytic systems $Fe(acac)_3$–$(Ph_2P-CH_2)_2$–Et_2AlCl and $Co(acac)_2$–$(Ph_2P-CH_2)_2$–Et_2AlCl. Three of the seven unsaturated NBD dimers, namely compounds (II) (X), and (XIV), whose molecules contain the norbornene fragment with *endo*-substituents, do not enter into the cyclodimerisation reaction with NBD.[97]

These results and also the regioselectivity of the addition of NBD to the "mixed" dimer (III), in which only the *exo*-disubstituted section of the molecule is involved, enabled the authors[97] to explain convincingly the inertness of the dimers (II), (X), and (XIV) by steric factors. It is noteworthy that the catalysts proposed in the above study make it possible to obtain one of the trimers (XLIII) by the direct cyclotrimerisation of NBD:[97,98]



Compounds (XLIII), (XLIV), (XLVII), and (XLVIII) have been formed as a result of the $[2_\pi + 2_\pi + 2_\pi]$-*exo,exo*-cycloaddition of the NBD molecule to the norbornene double bond of the corresponding dimer.

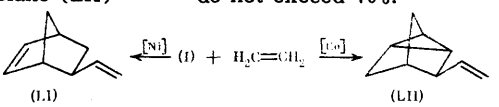
An interesting procedure for the synthesis of the NBD trimers by $[2_\pi + 2_\pi]$-*exo,endo*-cycloaddition has been proposed.[99] This reaction, which is accelerated by various rhodium complexes, namely $RhCl_3.4H_2O$, $Rh(acac)_3$, $[Rh(AcO)_2]_2$, etc., can serve as a convenient and promising method for the preparation of two previously unknown NBD trimers [(XLIX) and (L)] and two which were described previously[99] [(XLII) and (XLIV)].



V. THE CO-OLIGOMERISATION OF NORBORNADIENE WITH UNSATURATED COMPOUNDS

1. The Co-oligomerisation of Norbornadiene with Olefins

Olefins without electron-accepting substituents at the double bond are relatively inactive in cyclocodimerisation reactions with NBD. In particular, when ethylene reacts with NBD in the presence of zerovalent nickel complexes or the three-component cobalt catalyst $Co(acac)_2$–BPE–Et_2AlCl, the yields of 5-vinylnorbornene (LI)[100] and vinylnortricyclane (LII)[101–103] do not exceed 70%.

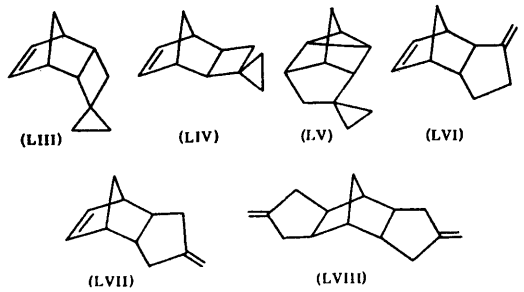


(LI) (LII)

There are literature data indicating the possibility of the involvement of propene in the reaction with NBD,[102] but there are no experimental details in the above communication

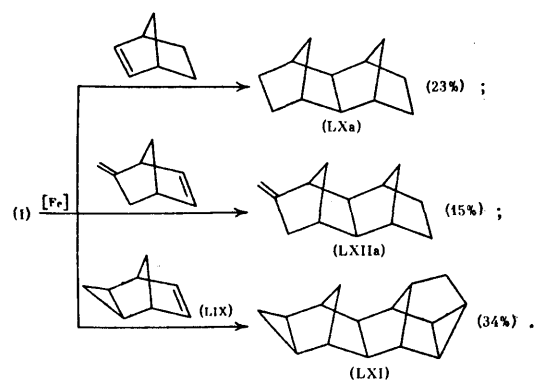
nor the physicochemical characteristics of the cyclic oligomers obtained.

In contrast to the simplest olefins, methylenecyclopropane readily reacts with NBD to form $[2_\pi + 2_\pi]$-, $[2_\pi + 2_\pi + 2_\pi]$-, and $[2_\pi + 2_\sigma]$-codimers. The mode of cyclocodimerisation is determined mainly by the nature of the catalyst. For example, the complex $Ni(COD)_2$ promotes the formation of the $[2_\pi + 2_\pi]$codimers (LIII) and (LIV), the $[2_\pi + 2_\sigma]$codimer (LVI), and the $[2_\pi + 2_\pi + 2_\pi]$codimer (LV),[105] while palladium catalyst afford the $[2_\pi + 2_\sigma]$co-oligomers (LVII) and (LVIII).[106,107] The selectivity in the formation of the codimer (LIII) can be raised to 100% by introducing into the catalyst an equimolar amount of PPh_3.[105]



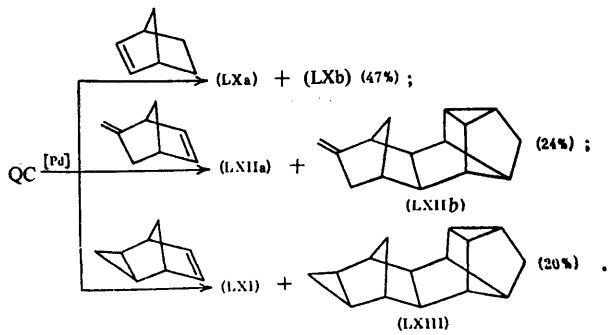
It was established subsequently[101,103,106,108] that cyclic olefins can also be involved in the reaction with NBD. A mixture of polycyclic hydrocarbons (yield ~22%) with a content of compound (VIa) of ~42%, was obtained from NBD and norbornene under the influence of the $Co(acac)_3$–BPE–Et_2AlCl catalyst.[101,103,106,108]

The codimerisation of NBD with norbornene, 5-methylenenorbornene and tricyclo[3.2.1.$0^{2,4}$]octa-6-ene (LIX) has been achieved using the $Fe(acac)_3$–BPE–Et_2AlCl catalytic system.[109]



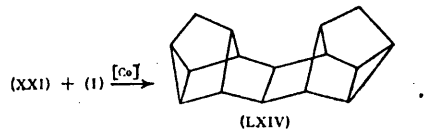
It is essential to note the high stereoselectivity in the activity of the catalytic system indicated. Only the *exo,exo*-codimers (LXa), (LXIIa), and (LXI) were obtained in all the experiments.

An alternative pathway to the synthesis of the hydrocarbons (LXa), (LXIIa), and (LXI) has been described.[96] A distinct characteristics of this method involves the use as the initial monomer not of BD but of its valence isomer—quadricyclane. The reaction is catalysed by the palladium complexes $Pd_2(DBA)_3$–$CHCl_3$ and $Pd(acac)_2$–PPh_3–$AlEt_3$.

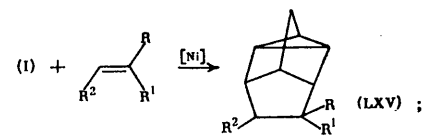


The scheme presented shows that the codimerisation of quadricyclane with cyclic olefins proceeds less selectively. Together with compounds (LXa), (LXIIa), and (LXI), the *exo,endo*-addition products (LXb), (LXIIb), and (LXIII) are present in the mixture. The ratio of the *exo,exo*- and *exo,endo*-isomers is approximately 2 : 3 and depends little on the structure of the cyclic olefins.

The cyclodimerisation of NBD with tetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]non-8-ene has been achieved recently in the presence of the catalytic system $Co(acac)_2$–BPE–Et_2AlCl.[110] Under optimum conditions, the yield of the octacyclic compound (LXIV) is 53% relative to the NBD which has reacted:



The introduction of electron-accepting substituents tends to increase the reactivity of olefins in relation to codimerisation with NBD, the reaction proceeding strictly stereoselectively in accordance with the $[2_\pi + 2_\pi + 2_\pi]$addition mechanism with formation of substituted tetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]nonanes (LXV):[8,111–114]

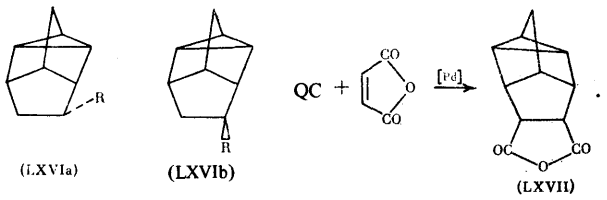


R = CN, CO_2Alk, COMe; R^1 = H, Me; R^2 = CO_2Me .

According to the literature,[11,111,119] such cyclodimerisation is catalysed by nickel complexes of different structure: $Ni(CO)_4$, $Ni(CO)_3(PPh_3)$, $Ni(CO)_2[P(OPh_3)]_2$, $Ni[P(OR)_3]_4$ (R = alkyl or aryl), $Ni(COD)_2$, $Ni(CH_2{=}CH{-}CN)_2$, $Ni(CN)_2.(PPh_3)_2$, and $Ni(acac)_2$-PPh_3–Et_2AlCl. The systems based on bis(acrylonitrile)nickel and $Ni(CN)_2(PPh_3)_2$ are the most active: the codimerisation of acrylonitrile with NBD take place at 60–80 °C with yields up to 95%.[14,112] Analogous results have been obtained using the $Co_2(CO)_8$–PPh_3 system.[112]

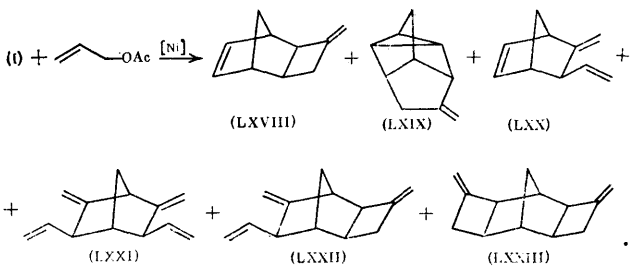
In terms of their reactivity in codimerisation with NBD, olefins with electron-accepting substituents can be arranged in the sequence acrylonitrile > crotononitrile > methacrylonitrile > dimethyl maleate.[14,112] The ratio of the *exo*-isomer (LXIIIa) and the *endo*-isomer (LXIIIb) in these experiments is determined by the nature of the solvent and the structure of the organophosphorus activators—ligands,[110] and is almost independent of the size of the ester substituent in acrylates.[8] The use of quadricyclane in this reaction instead of NBD increases the yield of the codimer but does not affect the ratio of the *exo*- and *endo*-isomers.[8]

Under mild conditions, quadricyclanes react with maleic anhydride to form the codimer (LXVII) in the presence of the catalytic system $(DBA)_2Pd_2.CHCl_3$–PPh_3.[9]



(LXVIa) (LXVIb) (LXVII)

An unusual reaction pathway is observed in the co-oligomerisation of norbornadienes with allyl ethers under the influence of the three-component catalytic system $Ni(acac)_2$–$P(OR)_3$–$AlEt_3$:[120,121]

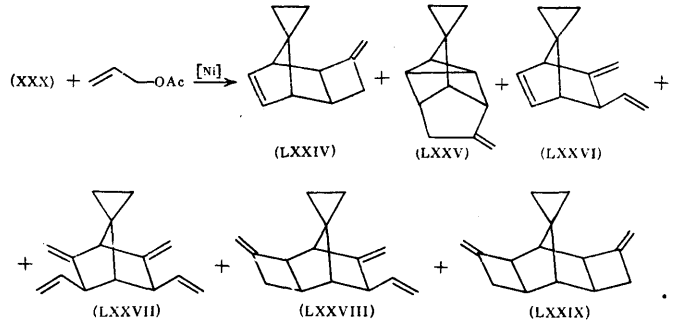


(LXVIII) (LXIX) (LXX) (LXXI) (LXXII) (LXXIII)

It follows from the above scheme that the reaction formally involves the addition to NBD of one or two allene molecules, but the process proceeds in a complex manner as can be seen from the structure of the products (LXX), (LXXI), and (LXXII).

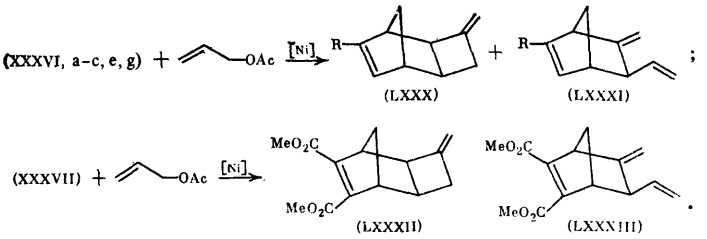
The isomeric composition of the co-oligomers depends on temprature and the nature and structure of the organophosphorus ligand. At room temperature the main reaction products are the cyclic compounds (LXXVIII) and (LXIX). The most active catalysts have been obtained using alkyl phosphates as the promoting agents.

The co-oligomerisation catalysts are relatively insensitive to the structure of the substituents in the NBD molecule. For example, 7-spiro-cyclopropanenorbornadiene (XXX) reacts with alkyl acetate to form six isomers in an overall yield of ~80%.[120,121]



(LXXIV) (LXXV) (LXXVI) (LXXVII) (LXXVIII) (LXXIX)

The composition of the reaction product simplifies when 2- and 2,3-substituted NBD are used.

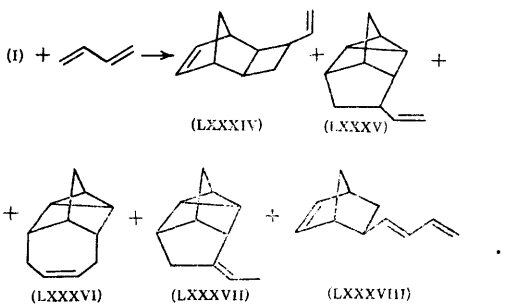


(LXXX) (LXXXI) (LXXXII) (LXXXIII)

The reaction indicated is general and can serve as a promising method for the synthesis of polycyclic hydrocarbons containing the methylenecyclobutane group, which are otherwise difficult to obtain.[122]

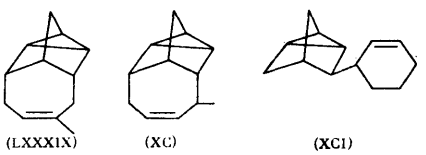
2. The Co-oligomerisation of Norbornadiene with Dienes

The addition of dienes to NBD in the presence of metal complex catalysts based on nickel, iron, cobalt, and manganese compounds has been investigated in detail by Italian workers. Thus the codimerisation of butadiene and NBD results in the formation of a mixture of the polycyclic hydrocarbons (LXXXIV) and (LXXXV) in a high yield.[55,79,101,123,124]



(LXXXIV) (LXXXV) (LXXXVI) (LXXXVII) (LXXXVIII)

The codimer of 5-butadienylnorborn-2-ene (LXXXVIII) is obtained in a high yield and a selectivity up to 94% in the presence of the $Co(acac)_3$-1,2-bis(diphenylphosphino)ethane–$AlEt_3$ catalytic system.[79,125–127] The use of Et_2AlCl as the reductant tends to alter the direction of the reaction towards the formation of the codimer (LXXXVI).[101,128] The same three-component catalytic system has been used in the codimerisation of NBD with isoprene, piperylene, and cyclohexa-1,3-diene in order to obtain compounds (LXXXIX)–(XCI) respectively.[101,129–132]

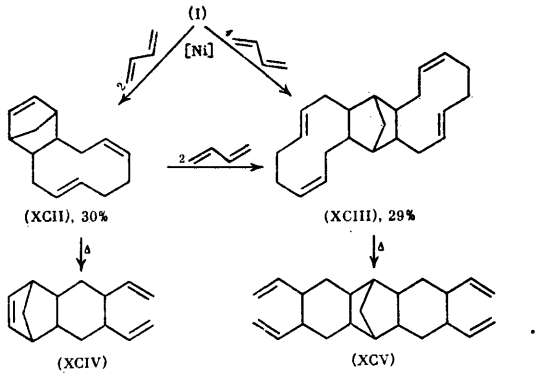


(LXXXIX) (XC) (XCI)

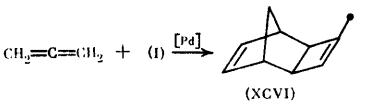
According to Ref.133, tetracyclo[5.4.0.$0^{6,10}$.$0^{9,11}$]undec-3-ene (LXXXVI) can be obtained with a high selectivity from NBD in budadiene in the presence of iron complexes.

The best method of synthesis of compound (LXXXIV) (in a yield of 90%) consists in the $[2_\pi + 2_\pi]$cycloaddition of butadiene to NBD in the presence of the complex $(C_5H_5)Ti(CH_2Ph)_3$ at 135–155 °C.[134–136]

The mixed cyclo-oligomerisation of NBD and butadiene taken in molar proportions of 1 : 6 in the presence of the three-component system $Ni(acac)_2$–$AlEt_2(OEt)$–tris(*o*-biphenylyl) phosphite as the catalyst, results in the formation of compounds (XCII) and (XCIII), which isomerise at 150 °C to compounds (XCIV) and (XCV):[137]



The reaction of 1,2-dienes with NBD and its derivatives is extremely interesting. In the presence of zerovalent palladium complexes,[138,139] the unsubstituted allene reacts with NBD to form exclusively the $[2_\pi + 2_\pi]$cycloaddition product (XCVI):



Under the influence of the three-component catalyst $Co(acac)_2$–PPh_3–Et_3AlCl, NBD and compound (XXX) react with allene via both $[2_\pi + 2_\pi]$ and $[2_\pi + 2_\pi + 2_\pi]$ mechanisms:[140]

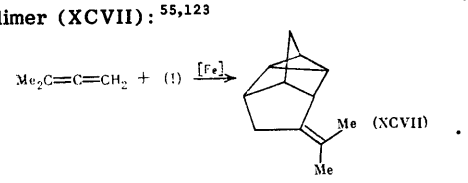
$$(I) + CH_2{=}C{=}CH_2 \xrightarrow{[Co]} \underset{85\%}{(LXIX)} + \underset{15\%}{(LXXII)} \ ;$$

$$(XXX) + CH_2{=}C{=}CH_2 \xrightarrow{[Co]} \underset{85\%}{(LXXV)} + \underset{19\%}{(LXXIX)} \ .$$

The main reaction product is a hydrocarbon with the deltacyclane structure, (LXIX) or (LXXV). The co-oligomers (LXXIII) and (LXXIX) are apparently formed in steps but the intermediate $[2_\pi + 2_\pi]$codimers were not detected in the reaction mixture.

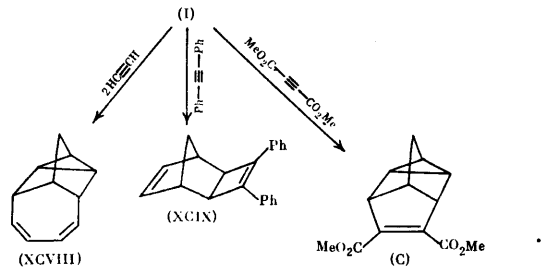
A very complex composition of the products (up to 10 isomers) has been obtained in the co-oligomerisation of NBD with 1,1-dimethyl-, 1-cyclopropyl-, and 1-phenyl-allenes with cyclonona-1,2-diene. Their reactivity is inferior to that of allene, which is indicated by the high yield of the co-oligomers (~80%).[140]

The catalyst obtained by reducing $Fe(acac)_3$ with diethylaluminium chloride directs the reaction of NBD with 1,1-dimethylallene towards the selective formation of the $[2_\pi + 2_\pi + 2_\pi]$codimer (XCVII):[55,123]

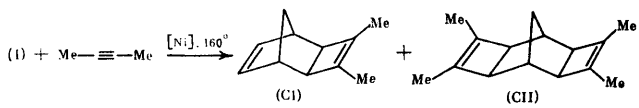


3. The Co-oligomerisation of Norbornadiene with Acetylenes

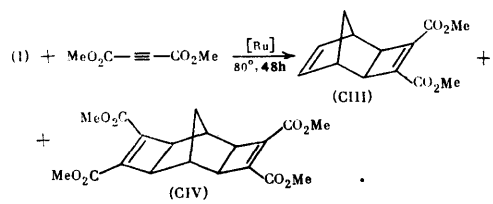
According to Schrauzer and Glockner,[112] the nickel complexes $Ni(CO)_2(PPh_3)_2$ and $Ni(CN)_2(PPh_3)_2$ catalyse the cycloaddition of acetylene, diphenylacetylene, and dimethyl acetylenedicarboxylate to NBD at 120 °C with formation of compounds (XCVIII), (XCIX), and (C):



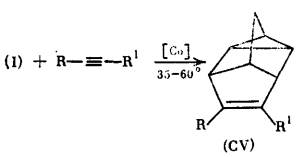
The use of tetrakis[tri(2-ethylhexyl) phosphite]nickel increases the yield of compound (XCIX) to 74%.[141] In the presence of the same catalyst, but-2-yne reacts vigorously with NBD via the $[2_\pi + 2_\pi]$ mechanism, affording the tri- and tetra-cyclic hydrocarbons (CI) and (CII):



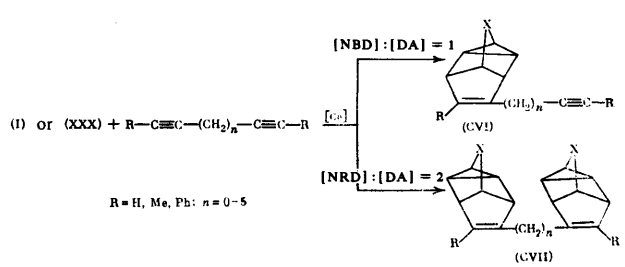
NBD and dimethyl acetylenedicarboxylate interact via an analogous mechanism in the presence of the ruthenium complex $[H_2Ru(PPh_3)_4]$, forming the *exo*-co-oligomers (CIII) and (CIV):[142]



Cobalt-containing systems, obtained by reducing $Co(acac)_2$ with Et_2AlCl in the presence of biphosphine, exhibit exceptionally high catalytic activity in the $[2_\pi + 2_\pi + 2_\pi]$cycloaddition of NBD to acetylene.[101,143–145] The highest yields of deltacyclene derivatives were obtained in experiments with acetylene and phenylacetylene.

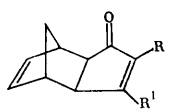


A novel pathway leading to the bisdeltacyclene structures (CVII), which are otherwise difficult to obtain, arises from the co-oligomerisation of NBD and compound (XXX) with diacetylenes (DA) under the influence of the $Co(acac)_2$–PPh_3–Et_2AlCl catalytic system:[140]



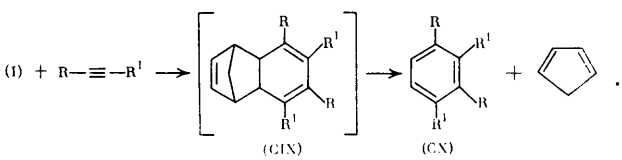
The yields of compounds (CVI) and (CVII) depend significantly on the distance between the acetylene fragments in DA and on the nature of the substituent, reaching 80% for $n \geq 3$ and R = H or Me. By altering the molar ratio of the monomers, the process can be directed towards the formation of the monoadduct (CVI) or the diadduct (CVII). In the reaction involving diphenyldiacetylene, the yield of compound (CVII) does not reach 10%, while 1,3-diacetylene fully polymerises under the reaction conditions.[140]

In the presence of the complexes $Co_2(CO)_8$ or $Fe(CO)_5$, the main products of the codimerisation of NBD with acetylenes are the cyclopentenone derivatives (CVIII).[146,147]



(CVIII)

The use of zerovalent iron and palladium complexes as catalysts of the cyclocodimerisation of NBD with acetylenes leads to the formation of 1,3-di- and 1,2,3,4-tetra-substituted benzenes (CX):[148,149]



(CIX) (CX)

Carbonaro et al.[148] and Suzuki et al.[149] postulated the intermediate formation of the thermodynamically unstable intermediate (CIX), which decomposes into cyclopentadiene and compound (CX).

Thus the co-oligomerisation of NBD with olefins, 1,2- and 1,3-dienes, and acetylenic hydrocarbons under the influence of nickel, palladium, cobalt, and iron complexes can serve as an effective method of the single-state synthesis of mono- and bis-tetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]nonane (deltacyclane), tricyclo[4.2.1.$0^{2,5}$]nonane, and tetracyclo[5.4.0.$0^{6,10}$.$0^{9,11}$]-undecane hydrocarbons.

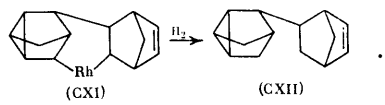
VI. THE MECHANISM OF THE DIMERISATION AND CODIMERISATION OF NORBORNADIENE

The cyclodimerisation and cyclocodimerisation of NBD and its derivatives belong to the so-called pericyclic reactions prohibited by symmetry rules. However, they are catalytically allowed although the causes of this fact have not so far been elucidated.[150–157]

In 1967 Mango and Schachtschneider[150] proposed a theory according to which the interaction of a transition metal atom with olefins entails a change in the symmetry of the highest occupied orbitals and the cyclisation reaction becomes allowed. There exists also another view on the role of the metal in catalysis according to which the role of the neutral catalyst atom consists in reducing the activation energy for the prohibited reaction and not in changing the symmetry of the orbitals in the reactants.[155]

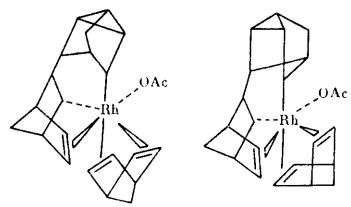
The experimental data accumulated permit the conclusion that the reactions indicated have a multistage mechanism. These include all the principal reactions of metal complex catalysis: coordination, oxidative addition, insertion, and reductive elimination.[9,154]

The key stage in the multistage mechanism of the cyclo-oligomerisation of olefins and dienes is the formation of metallocyclic compounds, which have been isolated and identified with the aid of modern physicochemical methods.[23,158–167] For example, the hydrogenation of a mixture of NBD and $(NBD)_2RhPF_6$ results in the formation of the hydrocarbon (CXII), for which one can postulate only one possible formation pathway—via the rhodacyclohexane organometallic compound (CXI):[162]



(CXI) (CXII)

The most reliable evidence for the multistage mechanism has been obtained in a study[7] of the isomerisation dimerisation of quadricyclane in the presence of rhodium catalysts. Organorhodium intermediate compounds (CXIII) and (CXIV), responsible for the formation of the molecules of NBD homo- and co-oligomers, have been observed and identified.



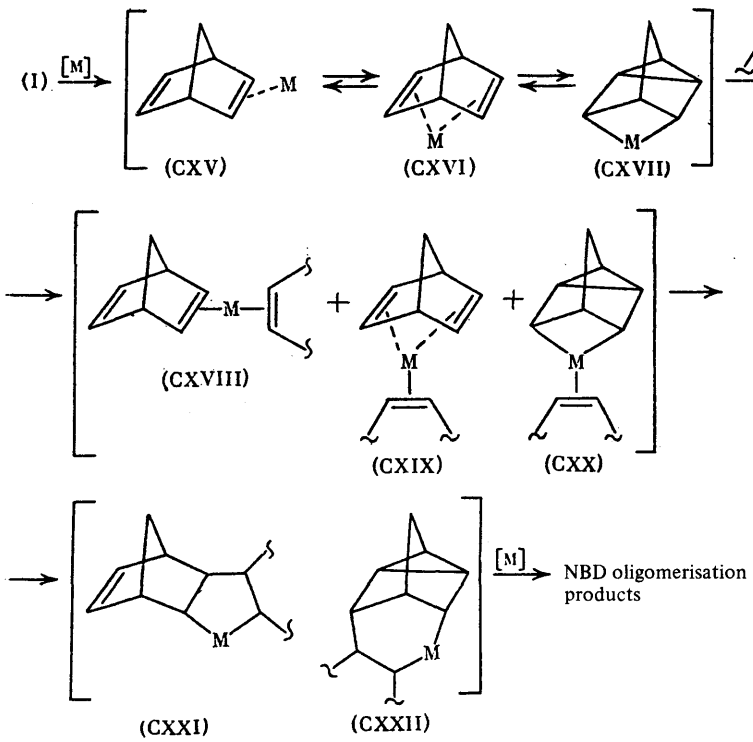
(CXIII) (CXIV)

Similar complexes were obtained in the reaction of hexafluorobutyne with NBD coordinated to rhodium via [$2_\pi + 2_\pi + 2_\pi$]cycloaddition. The structure of the rhodacyclobutane complex was determined by X-ray diffraction.[160] Analogous complexes are known for nickel, ruthenium, and iridium.[158, 164,165]

Experimental results[75,88] show that the stereospecific [$4_\pi + 4_\pi$]dimerisation of NBD proceeds at a single centre, whose role is fulfilled by a singly-charged rhodium or cobalt complex.

At the present time there is no single view concerning the individual stages of the mechanism of the dimerisation, trimerisation, and codimerisation of NBD, which can be accounted for by the lack of direct and complete experimental evidence for the validity of a particular mechanism. Despite this, when account is taken of the literature data,[101,168,169] it is possible to postulate what is to some extent a general and universal mechanism of the cycloaddition of NBD involving [$2_\pi + 2_\pi$], [$2_\pi + 2_\pi + 2_\pi$], and [$4_\pi + 4_\pi$] steps on the basis of key catalytic reactions: oxidative addition, insertion, and reductive elimination.

According to this possible mechanism (see Figure), NBD is initially coordinated to the metal with formation of complexes of three types: (CXI)–(CXVII). The equilibrium position in this system is determined by the number of free coordination sites at the metal atom, the nature of the ligand environment, and the charge on the transition metal. It is known that NBD interacts with electrophilic species, forming preferentially compounds containing the nortricyclane system. Consequently, the equilibrium for complexes whose central metal atom has a positive charge is displaced towards the formation of compound (CXVII) and, the greater the charge on the atom, the greater the shift of the equilibrium to the right. Successive coordination of the olefin leads to the intermediates (CXVIII)–(CXX), whose intramolecular reactions proceed either via the synchronous formation of metal–carbon and carbon–carbon σ-bonds or via the insertion of the olefin into the metal–carbon bond with formation of the metallocyclic compounds (CXXI) and (CXXII). The subsequent key stage in the NBD dimerisation and codimerisation reactions is the reductive elimination of the transition metal atom, which can again initiate a new catalytic cycle.



The possible mechanism of the dimerisation and codimerisation of norbornadiene.

The stereochemistry of the isomers formed should be fully determined by the charge on the central metal atom, its coordination number, and its ligand environment.

For the final elucidation of the mechanism of the NBD cycloaddition reaction, it is essential to carry out kinetic studies, to isolate the intermediates, and to investigate their properties in the greatest possible detail.

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During the preparation of the manuscript for the press, new communications and studies on the homo- and co-dimerisation of NBD and its derivatives in the presence of transition metal complexes were published.[170-173] The results of investigations of the codimerisation of NBD with cycloheptatriene under the influence of titanium-containing catalysts, with formation of new types of penta- and hexa-cyclic polycyclic compounds,[170] are of greatest interest. Several studies have been devoted to the cyclodimerisation of NBD and of its 7-substituted derivatives via the $[4_\pi + 4_\pi]$cycloaddition mechanism.[171-173]

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