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Norbornene, norbornadiene and their derivatives: promising semi-products for organic synthesis and production of polymeric materials

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The methods for synthesis of promising norbornene monomers from norbornadiene and quadricyclane are summarized. A strategy for their synthesis is discussed, combining theoretical and experimental approaches to the selection of catalysts and the conditions for carrying out stereoselective reactions. The mechanisms of catalytic reactions of synthesis of norbornene monomers, as well as the progress in the macromolecular design of functional polymeric materials based on them, are considered. The data on industrial processes of production of polynorbornenes and areas of their use are presented. The bibliography includes 297 references.

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1. Introduction

Norbornene (NB), norbornadiene (NBD) and their derivatives are becoming increasingly important in various fields of human activity, and new areas of their use are regularly identified. Over more than 60-year history, these compounds have found application in medicine and agriculture, rocket technology and the production of polymeric materials with unique properties, microelectronics, as solar energy converters and efficient gas separation membranes. By 2018, the number of publications and patents related to the production and use of NB and NBD derivatives exceeded 30 thousand. It can be said that compounds comprising these structures, due to their unique structure, become important objects of modern chemistry and chemical engineering.

Norbornene, norbornadiene and some of their simplest derivatives have a reliable resource base. Their sources are

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large-tonnage products of oil refining, such as 1,3-cyclopentadiene (CPD), acetylene, alkenes and alkadienes of various structures. The CPD production can easily be combined with the production of other products, in particular, ethylene. At the present time, not all CPD finds qualified application; therefore, the search for new promising ways to use it is especially relevant.

Nevertheless, despite the extremely rich synthetic possibilities, the practical use of NB and NBD derivatives as substrates for various purposes is rather limited. The structural features of the norbornene carbocyclic cage imply the presence of all types of isomerism in such compounds: skeletal, regio-, stereo- and enantioisomerism. In actual syntheses, this often leads to the formation of a mixture of isomers. Difficulties of separation and analysis of isomeric products, problems of rational use of reagents in many respects limit the large-scale use of NB and NBD. At the same time, this circumstance makes the objects in question very convenient for research and development of approaches to solving the problem of selectivity at various levels.

Until 2000, the synthesis of NB- and NBD-based carbocyclic compounds has been largely carried out empirically, by an intuitive selection of catalysts, ligand environment and reaction conditions. Only in the last 15–20 years, systematic studies of the kinetics and reaction mechanisms involving NB and NBD, as well as the application of quantum chemistry methods for such objects and processes, have begun. The combination of these rapidly developing areas now allows us to purposefully develop and optimize the reaction conditions for obtaining individual products and related materials with special properties.

Further development of this strategy involving a combination of theoretical and experimental approaches with the obligatory presence of feedback will make it possible not only to reduce the complexity and optimize experimental studies, but also to better understand the mechanisms of the processes under study. At the same time, attempts have been made to develop heterogeneous catalysts, which have undoubted technological advantages over homogeneous ones. Only the first steps have been taken on this path, and researchers will have to overcome many problems, both theoretical and experimental.

Since the number of works addressing the chemistry of NB and NBD derivatives is extremely large and the synthetic aspects have been already reflected in a significant number of fundamental reviews[1–8] and monographs,[9–12] this article focuses on the most important, from our point of view, areas and trends in the development of chemistry of carbocyclic compounds of the norbornene series. In addition, the review mainly considers reactions aimed at the production and use of monomers and intermediates that retain the active double bond in the norbornene ring, including polymerization reactions with its participation.

Metal complex catalysis is extremely attractive for solving these problems. Its principles and methods as applied to NB, NBD and their derivatives and a detailed study of reaction mechanisms allow one to control the structure and composition of regio- and stereoisomers, increase the range of compounds of this unique class and make their production technologically and economically feasible.

Norbornene and norbornadiene are active monomers that can polymerize by different mechanisms depending on the nature of the selected catalyst. As a result, metathesis, addition and isomerization polymerization of NB derivatives can lead to polymers with different structures of the backbone and side groups exhibiting desired physicochemical properties. The interest of researchers in this area of polymer chemistry has significantly intensified over the past decade. Most relevant studies deal with the development of new highly active and selective catalysts capable of conducting controlled, or 'live', polymerization. The advent of these catalysts has stimulated work on macromolecular design with the targeted production of new functional (co)polymers, nanostructured and composite materials with a wide range of practically valuable properties. Methods of synthesis of new active NB monomers, tricyclononenes, from NBD and quadricyclane (Q) have been developed. The resulting TCNs turned out to be a source of polymers exhibiting valuable properties of photoresists and gas separation membranes.

The following abbreviations are used in this review:

AA — allyl acetate;
acac — acetylacetonate;
AF — allyl formate;
All — allyl;
AP — addition polymerization;
APNB — polynorbornene synthesized by addition polymerization;
BBC — bottle-brush copolymers;
BBP — bottle-brush polymers;
Binor-S — heptacyclo[8.4.0.0^{2,12}.0^{3,8}.0^{4,6}.0^{5,9}.0^{11,13}]-tetradecane;
COC — cycloolefin copolymers;
COD — 1,5-cyclooctadiene;
COE — cyclooctene;
COP — cycloolefin polymers;
Cp — cyclopentadienyl;
Cp* — pentamethylcyclopentadienyl;
CPD — 1,3-cyclopentadiene;
Cy — cyclohexyl;
DCE — 1,2-dichloroethane;
DCPD — dicyclopentadiene;
DFT — density functional theory;
dppe — 1,2-bis(diphenylphosphino)ethane;
EA — ethyl acrylate;
Fc — ferrocenyl;
Gr-1, Gr-2, Gr-3 — Grubbs catalysts of the first, second and third generation;
Gr-H-1, Gr-H-2 — Hoveyda–Grubbs catalysts of the first and second generation;
MA — methyl acrylate;
MAO — methylaluminoxane;
MAP — monoalkoxypyrrolide ligand;
MCP — methylcyclopropane;
MD — molecular dynamics method;
Mes — mesityl (2,4,6-trimethylphenyl);
MMAO — modified methylaluminoxane;
MMD — molecular mass distribution;
MPNB — polynorbornene synthesized by metathesis polymerization;
MVK — methyl vinyl ketone;
NB — norbornene;
NBD — norbornadiene;
NHC — N-heterocyclic carbenes;
P — phosphorus-containing ligand;
PCO — polycyclooctene;
PDMS — polydimethylsiloxane;

PNB — polynorbornene;
POSS — polyhedral oligomeric silsequioxanes;
ROMP — ring-opening metathesis polymerization;
SEPR — synthetic ternary ethylene–propylene rubbers;
SiNB — norbornenes with silyl substituents;
SiNBD — norbornadienes with silyl substituents;
SI-ROMP — surface-initiated ROMP;
SiTCN — tricyclononenes with silyl substituents;
TBA — *tert*-butyl acrylate;
TCD — tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-4-ene;
TCN — tricyclononene;
Tf — triflyl (trifluoromethanesulfonyl);
TON — catalyst turnover number;
Q — quadricyclane.

2. Theoretical approaches to analysis of reactions involving norbornene and norbornadiene derivatives

Currently, theoretical studies often precede practical syntheses involving NB. The early theoretical studies addressing NB chemistry were aimed at explaining the observed experimental facts. Along with these works, studies are available where the experiment is preceded by quantum chemical calculations, which optimize the range of objects and predict the main reaction paths and probable reaction conditions and selectivity. Similar calculations pertain to both catalytic and non catalytic reactions.

Symbiosis of such approaches is presented, for example, for noncatalytic diene synthesis that affords unique carbocyclic structures.[13–20] Despite the apparent simplicity, the patterns of this reaction are far from being always obvious. In particular, the reaction of NB with CPD can give four stereoisomers of tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-4-ene (TCD) (Scheme 1).[21]

For each of the four stereoisomers, the thermodynamic and kinetic characteristics at 498 K have been calculated by the density functional theory (DFT) method (DFT-PBE/6-31G*) (Table 1). The revealed thermodynamic preferences correlate with structural features of molecules caused by the stereochemistry of the reaction of their formation. In particular, the TCD-a and TCD-b codimers form when the CPD molecule approaches the NB double bond from the *exo*-position. Conversely, the *endo*-attack leads to TCD-c and TCD-d. This should be reflected in the activation parameters of the studied reactions.

Scheme 1

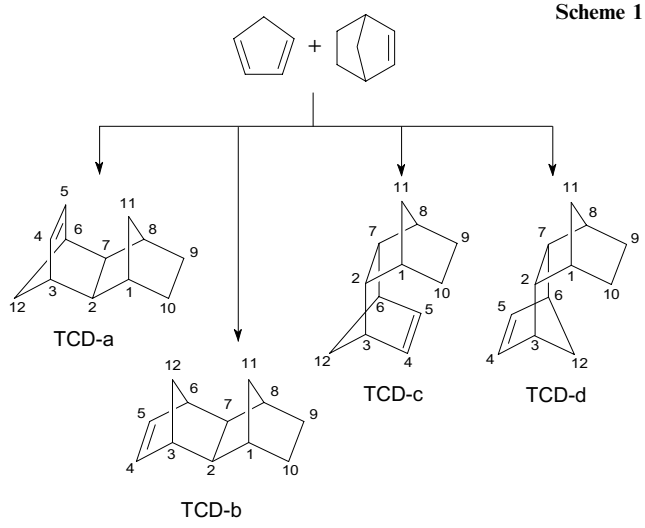


Table 1. Thermodynamic and activation characteristics (in kcal mol^{-1}) of the copolymerization of norbornene and cyclopentadiene according to DFT-PBE/6-31G* (Ref. 21).

Copolymerization product	$\Delta^{\neq}G_{498}$	$\Delta_rG^{\circ}_{498}$	$\Delta^{\neq}H_{498}$	$\Delta_rH^{\circ}_{498}$
TCD-a	35.845	0.589	14.383	−24.008
TCD-b	38.698	0.362	17.630	−24.014
TCD-c	45.083	4.402	22.989	−20.761
TCD-d	47.287	2.986	26.182	−21.892

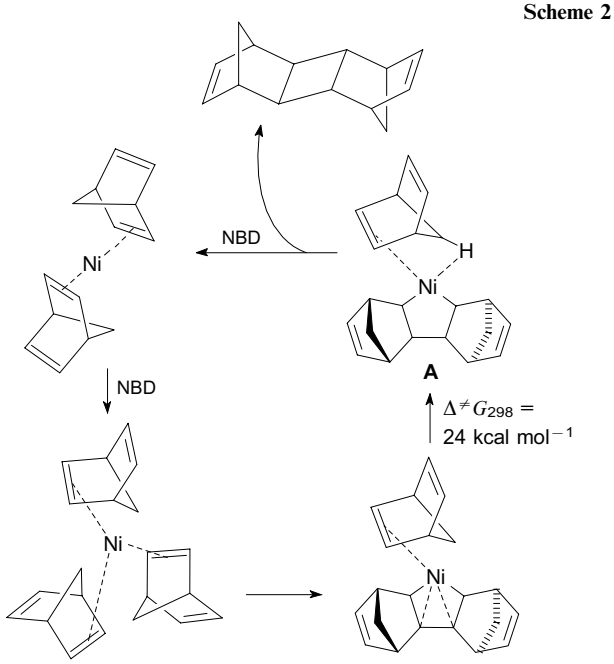
It follows from Table 1 that the energy barrier for the *exo*-isomers TCD-a and TCD-b is significantly lower (by 10 – 12 kcal mol^{-1}) than that for the *endo*-isomers, and this parameter will determine the stereochemistry of the entire reaction. The TCD isomers form through four parallel second-order reactions, each of which is simple. The predicted selectivity of the process, calculated as the ratio of the rate constants of individual steps, corresponds to the formation of 94.3% of TCD-a and 5.7% of TCD-b.[21] Experimental results turned out to be extremely close to the quantum chemical calculation data. In the temperature range 200 – 250 °C, TCD-a and TCD-b are formed in 93.5% to 6.5% ratio.[21] In the course of experiment, this ratio does not change, which is typical of parallel reactions of the same kinetic order.

By the moment of writing this review, a sufficient number of examples of the application of quantum chemical approaches to the study of catalytic processes involving NBD and NB derivatives have appeared. In particular, DFT modelling of the reaction paths involving the formation of Ni complexes containing two to four NBD ligands made it possible to determine the most probable mechanism of the formation of the *exo*–*trans*–*exo* NBD dimer.[22] The rate-limiting step is the formation of 'unsaturated' nickelacyclopentane complex **A** with an agostic hydrogen bond (Scheme 2).[22] The free activation energy of the process ($\Delta^{\neq}G_{298}$), calculated from the kinetic and theoretical data, is 22 ± 2.5 and 24.0 kcal mol^{-1}, respectively, which can be evidence of the correctness of the suggested mechanism.[22] The formation of the *cis*-dimer is energetically unfavourable. This fact explains the absence of *cis*-dimers among the reaction products. For comparison, the free activation energy of the thermal (noncatalytic) cyclodimerization of NBD (Ref. 23) is 36.7 – 57.5 kcal mol^{-1}, depending on the dimer structure.

The preference of the η^2-*exo*-coordination of NBD in the *cis*–*trans* isomerization reaction of the allyl ligand in bis(η^3-allyl)nickel has been reported.[24] This reaction exemplifies the primary interaction of NBD with the catalyst precursor.

The formation of the heptacyclic NBD dimer — heptacyclo[8.4.0.0^{2,12}.0^{3,8}.0^{4,6}.0^{5,9}.0^{11,13}]tetradecane (Binor-S) — in the presence of cationic Co^{I}, Rh^{I} and Ir^{I} complexes has been studied by a quantum chemical method (Ref. 25). The rate-limiting reaction step is the formation of the first C – C bond. The free activation energies are estimated at 13.7, 22.1 and 28.2 kcal mol^{-1} for Co^{I}, Rh^{I} and Ir^{I}, respectively. The formation of the first C – C bond is also rate-limiting in

Scheme 2



the formation of the *endo*–*endo* dimer[26] on the cationic $[Fe^{II}Cl]^+$ complex.

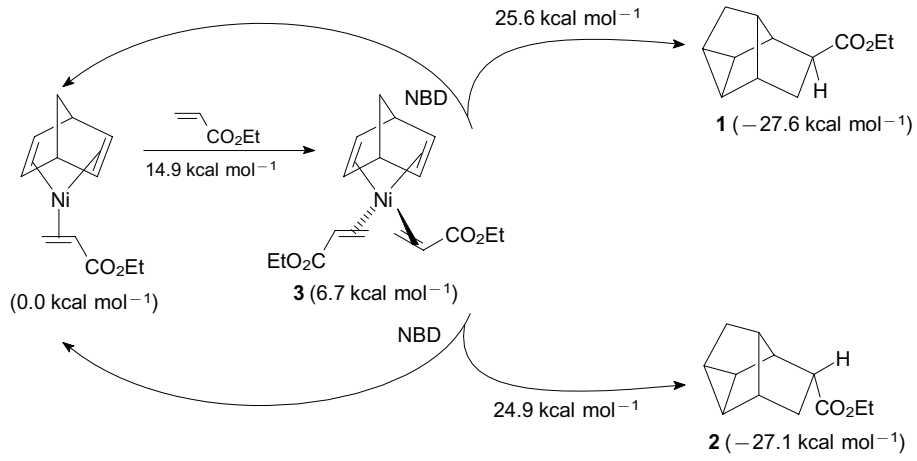
Continuous improvement of physicochemical methods more and more often makes it possible to observe intermediates directly in the course of a catalytic reaction. This raises the question of their role in catalysis. In particular, in the course of catalytic NBD dimerization where η^3-allyl nickel complexes Ni(η^3-All)$_2$ (All = C_3H_5, 1-MeC_3H_4, 2-MeC_3H_4) were used as precursors, the formation of a paramagnetic Ni^I complex has been detected (Ref. 27). It is believed that the Ni^I complex forms through complex transformation of bis(η^3-allyl)nickel and can be of both the allyl and hydride nature. The use of theoretical methods (PBE/TZ2P) made it possible to verify the assumption about the participation of the Ni hydride complex in the NBD dimerization.[28,29] It has been demonstrated that the Ni(H)(η^4-NBD) complex can hypothetically act as a catalytically active species; however, the corresponding free activation energies are rather high (37.7 and 47.5 kcal mol^{-1} for the *exo*–*trans*–*exo*- and *exo*–*trans*–*endo*-dimers, respectively). Nevertheless, final conclusions are currently premature.

There are also other examples where it has been theoretically demonstrated the preferable formation of a certain stereoisomer in cycloaddition reactions involving NBD. In particular, the codimerization of NBD with acrylates leads to the formation of *exo*- and *endo*-cycloadducts (**1** and **2**, Scheme 3). The reaction is complicated by the occurrence of the side NBD dimerization. DFT modelling of this reaction with ethyl acrylate (EA) as an example[30] revealed the common diolefin intermediate Ni(η^4-NBD)(EA)$_2$ (**3**) in the paths to isomers **1** and **2** (see Scheme 3, ΔG_{323} values are given). The formation of the first C–C bond is the rate-limiting step of the mechanism, while the formation of the next C–C bonds require noticeably lower energy inputs. According to the mechanism, the kinetic equation should be of first order in acrylate and catalyst, which is completely consistent with the experimental data. The formation of the *endo*-isomer is 0.7 kcal mol^{-1} more favourable, which leads to a slight predominance of this isomer observed in the experiment.[31]

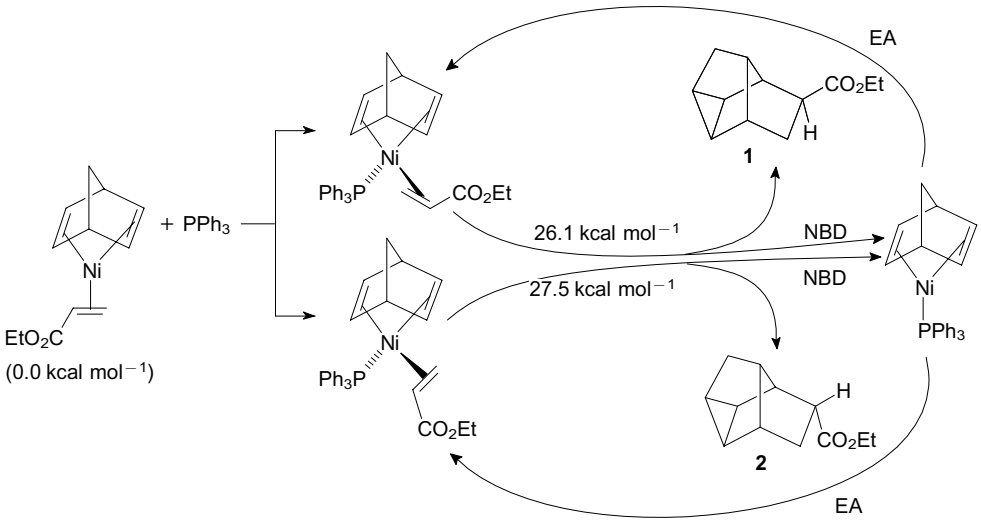
The effect of phosphine addition on the regioselectivity of codimerization of acrylates with NBD is of interest. The introduction of triphenylphosphine changes the ratio between stereoisomers **1** and **2** and completely suppresses the side NBD dimerization.[32] Quantum chemical calculations have demonstrated that the presence of PPh_3 in the system leads to the appearance of alternative paths of formation of products of EA cycloaddition to NBD (Scheme 4, ΔG_{323} values are given).[33] As distinct from the mechanism shown in Scheme 3, in the presence of PPh_3 the formation of stereoisomers **1** and **2** occurs through different intermediates. The difference between the activation energies for the formation of the *exo* and *endo* cycloadducts is 1.4 kcal mol^{-1}, which explains the higher reaction selectivity towards *exo*-isomer **1**. The absence of dimers at PPh_3 : Ni $\geqslant$ 1 can be explained by an increase in the activation barrier to the NBD dimerization channel as compared to the channels of formation of cycloadducts **1** and **2**. For example, the formation of NBD dimers in a phosphine-free system requires the overcoming of a maximal activation barrier of 25.5 kcal mol^{-1} ($\Delta^{\neq}G_{323}$), while in the presence of PPh_3, this barrier is 30.8 kcal mol^{-1}.

Diphosphine additives have a similar effect. However, in this case, the yield of products is sharply reduced. Theoretical calculations of the probable intermediates of the cyclo-

Scheme 3



Scheme 4



addition of methyl acrylate (MA) to NBD made it possible to explain the dependence of the product yield on the diphosphine structure.[34]

DFT calculations of the mechanism of the Ru-catalyzed [2 + 2]-cycloaddition of $PhC{\equiv}CCO_2Et$ to NBD and its 7-substituted derivatives demonstrate that the activation barrier to the formation of the second C—C bond is significantly lower than the barrier to the formation of the first C—C bond (9.3 – 9.8 against 25.9 – 27.6 kcal mol^{-1}).[35]

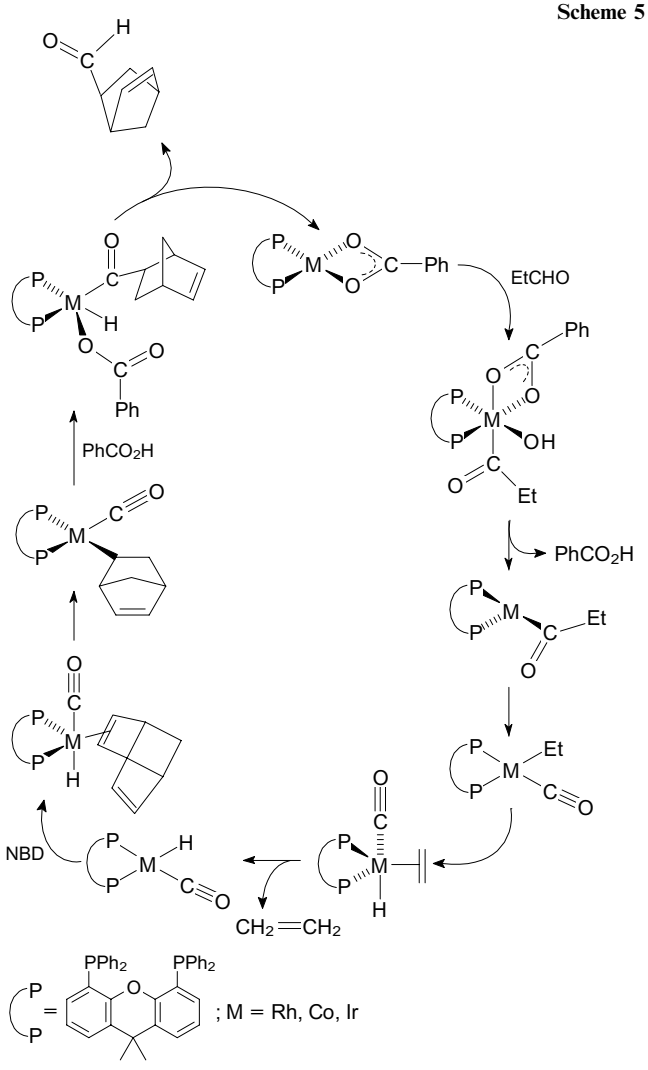
There are examples of theoretical studies of NBD functionalization. The mechanism of the important transfer hydroformylation reaction involving NBD has been suggested on the basis of DFT calculations.[36, 37] In contrast to the 'classical' hydroformylation, in this process the formyl group is transferred from the substrate containing the HCO group to the alkene. The mechanism shown in Scheme 5,[36] involves the deformylation of an aldehyde molecule and the stages of hydrogenation and carbonylation of the NBD molecule. Despite the similarity of the mechanisms, the rate-determining states and their energies for the paths catalyzed by Rh, Co and Ir complexes are different.

Detailed theoretical analysis of the addition polymerization of NB on the cationic Pd allyl complex has been reported.[38] It has been shown that electron-withdrawing substituents in the allyl group can noticeably affect the ratio of the activation energies of the chain initiation and propagation stages.

The ring-opening metathesis polymerization mechanism of NBD in the presence of molybdenum alkylidene complexes has been suggested.[39] The stage of formation of the molybdenacyclobutane complex has the highest energy barrier. The stereochemistry is influenced by bulky ligands in the Mo complex. The same reaction, but with the participation of NB in the presence of Re nitrosyl complexes, have been studied.[40] DFT calculations have demonstrated the preference of the 'imine' route of the mechanism. It has been revealed[41] that the gap between the frontier orbitals of the NBD molecule and Ni^{II} diimine complexes correlates with their catalytic activity in the homopolymerization of NB.

Complex studies of the copolymerization of ethylene with NB and its derivatives in the presence of Ti complexes[42, 43] have shown that the activation barriers of

Scheme 5



NB – ethylene copolymerization are noticeably higher than those of their polymerization.[44] The role of NB is mainly to decrease the barriers at the chain initiation and propagation stages.

The states pertaining to the formation of metallacycles with participation of NB and phebyl group have been considered.[44–47] It has been shown that, due to the cyclic structure of the NB molecule, the formation of the C–C bond between phenylboronic acid and NB in the Rh coordination sphere proceeds much faster with acyclic alkenes (*cis*-butene).[47]

The cycloaddition of quadricyclane to $Me_nCl_{3-n}Si$-substituted ethylenes has been studied in detail.[48] Different aspects of the [4+2]-cycloaddition of alkenes to cyclopentadiene to give NB and its derivatives have been theoretically studied.[49, 50]

3. Synthesis of norbornene derivatives from norbornadiene and quadricyclane

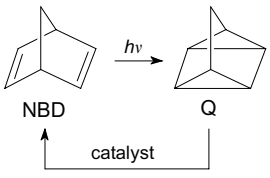
This review mainly addresses analysis of modern methods and approaches to synthesis of norbornene compounds — potential monomers and comonomers for further polymerization. Being clearly aware that the total number of reactions in which norbornenes and norbornadienes can participate is enormous, we have limited their range to those processes where the double bond in the norbornene moiety is retained. For NBD, these are predominantly [2+2]-cycloaddition reactions occurring only in the presence of catalysts, and for quadricyclane, these are noncatalytic transformations with various unsaturated compounds.

3.1. Valence isomerization of norbornadiene to quadricyclane

Norbornadiene is an interesting and in many ways unique molecule. This is a rare example of 1,4-diene hydrocarbons, in which this arrangement of double bonds is the most thermodynamically stable. Due to the rigid spatial structure provided by the methylene bridge (CH_2), the NBD molecule is highly strained. Its bond angles differ significantly from those characteristic of sp^3- and sp^2-hybridizations. The double bonds in NBD are homoconjugated. This is a special type of conjugation differing from 1,3-dienes or benzene, in which all the p_z orbitals participating in the conjugation are perpendicular to one common plane of the molecule. The p_z orbitals forming double bonds in NBD have only one spatial overlap region — under the molecule. As a result, double bonds acquire a higher reactivity. The combination of these properties allows NBD to participate in unique transformations, in particular, in valence isomerization.

Valence isomerization of NBD to quadricyclane is practically significant. Interest in this reaction is due to the possibility of accumulating light energy as a result of a cyclic process (Scheme 6).

Scheme 6



The photoreaction gives a metastable structure containing highly strained moieties: two cyclopropane rings and a cyclobutane ring. The consequence of this is an extremely high thermal effect of the inverse catalytic reaction: -110 kJ mol^{-1}.

TheNBD–Q system has been covered in fundamental reviews.[5, 8, 11] By now, a considerable amount of new results has been accumulated, which require separate systematization.[51–58] This system is being improved to optimize conditions of both the catalytic process and the photoreaction. New, more efficient sensitizers have been proposed, modified norbornadiene systems have been synthesized, and the characteristics of the selective catalytic reaction Q → NBD have been significantly improved. The technological foundations of this unique system have been created and are being improved, which makes it possible to synchronize both reactions and ensure the continuity of operation of the installation for converting light into heat energy.[59–62] Some of new studies have been devoted to quantum chemical estimates of the efficiency of this promising system.[63–66]

Thus, to date, practically feasible procedures for efficient synthesis of quadricyclane from NBD have been developed, which makes this substrate readily available. It can be expected that its large-scale use in synthetic chemistry will be fully justified.

3.2. Catalytic norbornadiene homodimerization

Norbornadiene dimers — strained high-energy hydrocarbons — can be used as components of high-density rocket propellants.[8–10] However, their synthetic capabilities have been realized only to a very little extent. This is due to the low selectivity of synthesis of individual isomers and difficulties of separating their mixtures. The structure of NBD dimers is shown in Fig. 1.

Norbornadiene is able to undergo cyclization reactions of various types.[1, 3, 8] The products of its cyclodimerization can be divided into four groups. The first three groups differ by the type of cycloaddition: [2π+2π], [2π+4π], and [4π+4π]. The fourth group comprises the products of skeleatal isomerization of dimers containing a strained cyclopropane moiety.

Dimers **4**–**9** of group I are the products of [2π+2π]-cycloaddition. These are pentacyclic compounds containing two double bonds and a cyclobutane moiety. Only *trans* dimers have been obtained experimentally: *exo*–*trans*–*exo*- (**4**), *endo*–*trans*–*endo*- (**5**) and *exo*–*trans*–*endo*-pentacyclo[8.2.1.1.^{4,7}.0^{2,9}.0^{3,8}]tetradeca-5,11-dienes (**6**). There are no indications of the existence of *cis*-isomers in the literature.

Dimers **10**–**13** of group II are the products of [2π+4π]-cycloaddition. These are hexacyclic compounds containing one double bond and a nortricyclic moiety: *endo*–*endo*- (**10**), *exo*–*exo*- (**11**), *exo*–*endo*- (**12**) and *endo*–*exo*-hexacyclo[9.2.1.0^{2,10}.0^{3,7}.0^{4,9}.0^{6,8}.]tetradec-12-enes (**13**).

Saturated heptacyclic dimers **14**–**17** of group III are products of the [4π+4π]-cycloaddition. The most interesting among them is Binor-S (**14**). Dimers **18**–**20** of group IV synthesized in the presence of $[Rh(PPh_3)_3Cl]$ are presumably derivatives of compound **12**.

The cyclodimerization of NBD always proceeds in the presence of a catalyst.[1, 3, 8, 11] These are, as a rule, complexes of Ni, Co, Fe and Rh in lower oxidation states. Separate examples of using Cr, Ti, Pd and Ir compounds are known.

NBD dimers that have norbornene moieties are the most interesting for further synthetic use. Among these compounds, best candidates are pentacyclic dimers **4**–**6**, which retain two active double bonds: one of them can be modified by known procedures, and the second bond can be used in polymerization reactions.

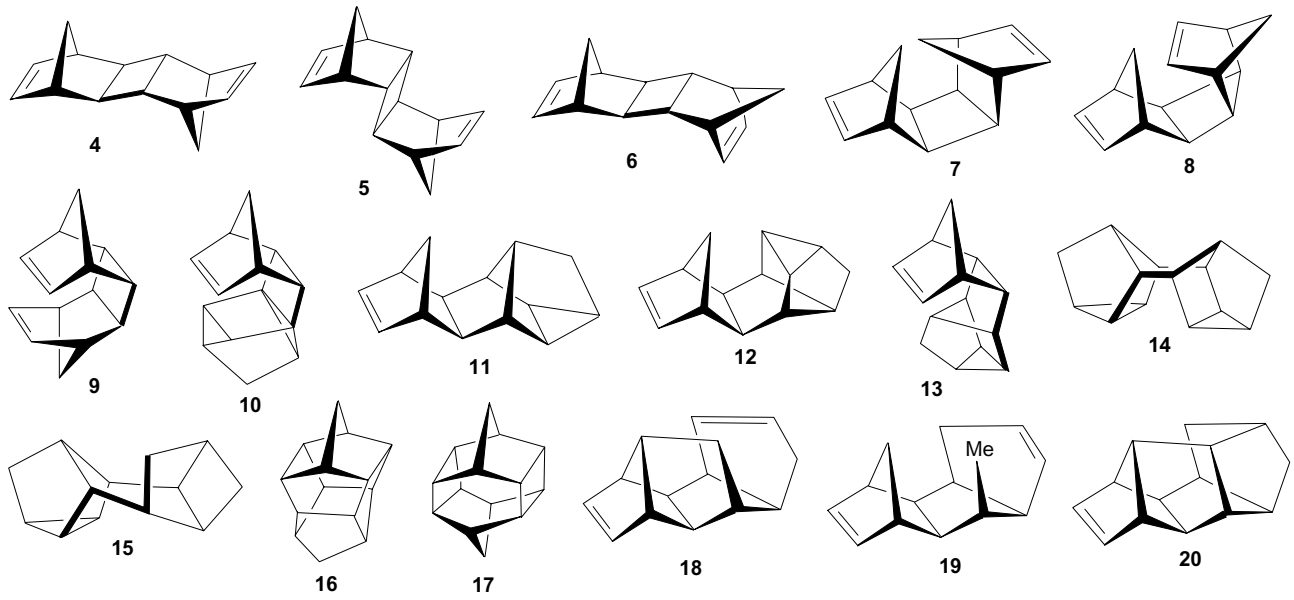


Figure 1. Structure of norbornadiene dimers.

Nickel catalysts are most selective for $[2\pi + 2\pi]$-cycloaddition. Quantum-chemical calculations performed for naked nickel (see Section 2) predict different paths of formation of dimers **4** – **6**. The most preferable among *trans* isomers are compounds **4** and **6**, whereas the formation of *cis* isomers **7** – **9** is impossible for both thermodynamic and kinetic reasons.

Experimental studies were completely consistent with theoretical calculations. Early studies dealt with the effect of the catalyst precursor structure [$(Ni(COD)_2$, $Ni(CH_2{=}CHCN)_2$, $Ni(CO)_4$, $Ni(\eta^3\text{-All})_2$, $Ni(\eta^5\text{-Cp})_2$ and others] on the reaction patterns. However, it has later been shown that, in the absence of stabilizing ligands in the reaction system, the same norbornadiene complexes $Ni(NBD)_n$ are formed. Such a 'ligand-free' catalytic system turned out to be the most efficient.[67] The formation rates of dimers **4** and **6** with inclusion of NBD molecules coordinated to the nickel complex are described by kinetic equations (1) and (2).

$$W_{\mathbf{4}} = k_{\mathbf{4}} C_{\mathrm{Ni}} C_{\mathrm{NBD}}^2 \quad (1)$$

$$W_{\mathbf{6}} = k_{\mathbf{6}} C_{\mathrm{Ni}} C_{\mathrm{NBD}} \quad (2)$$

where $k_{\mathbf{4}}$, $k_{\mathbf{6}}$ are the observed rate constants.

The formation rates of dimers **4** and **6** have different kinetic orders with respect to NBD, which is a rather rare phenomenon for isomers of similar structure.[68,69] The solvent has an effect on the product ratio and process rate. The observed rate constants $k_{\mathbf{4}}$ and $k_{\mathbf{6}}$ obey the Arrhenius equation, and the activation parameters are presented in Table 2.

The use of phosphine ligands significantly slows down the reaction as a whole and decreases its selectivity.

The mechanism of the catalytic action of nickel complexes has been studied.[31] The NBD molecule acts as an η^2- or η^4-coordinated ligand. The bidentate coordination of NBD is thermodynamically more favourable than the monodentate mode by the energy of double bond homoconjugation ($\sim$8.0 kJ mol^{-1}), which can be used for complex stabilization. Kinetic data point to the formation of three different nickel π-complexes with NBD (**21** – **23**) being at equilibrium (Scheme 7).

Table 2. Activation parameters of the norbornadiene cyclodimerization.[68]

Product	Solvent	Activation energy /kJ mol^{-1}	Preexponential factor	Activation entropy (see [a])
4	n-Nonane	33 ± 4	1.3×10^2 (see [b])	-209 ± 23
	THF	44 ± 5	1.0×10^3 (see [b])	-187 ± 10
6	n-Nonane	70 ± 7	5.6×10^7 (see [c])	-97 ± 10
	THF	51 ± 6	7.1×10^3 (see [c])	-171 ± 20

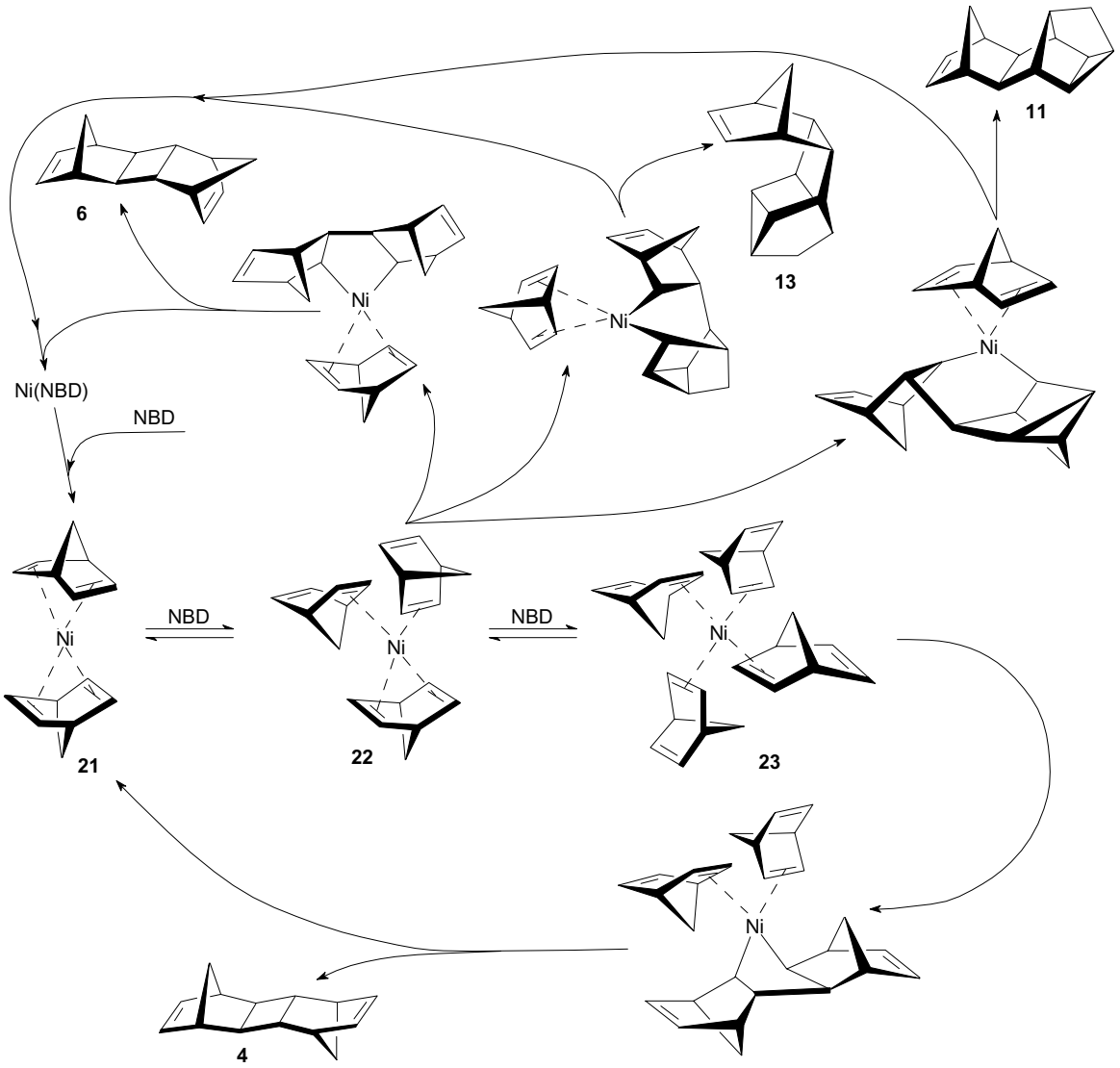
[a] In J mol^{-1} K^{-1}, [b] in litre^2 mol^{-2} s^{-1}; [c] in litre mol^{-1} s^{-1}.

When considering the stereochemistry of product formation, one should take into account not only the monodentate of chelating coordination mode of NBD to the nickel atom but also its *exo*/*endo* orientation. For the monodentate NBD coordination, the *exo* orientation is more sterically and thermodynamically preferable. The stereochemical analysis of various types of arrangement of the NBD molecule demonstrates that the *exo* coordination of four NBD ligands in the $Ni(NBD)_4$ complex is the only possible one. The oxidative addition of coordinated NBD molecules to the nickel atom leads to the formation of metallacyclic intermediates, their decomposition being the rate-limiting steps.

Blocking one coordination site at the nickel atom (ratio $PR_3 : Ni = 1 : 1$) changes the kinetic pattern of the process.[70] Phosphines with a large cone angle ensure a more compact *exo* coordination of NBD and an increase in the content of dimer **4**.

It follows from kinetic data that increasing NBD concentration and decreasing temperature lead to the preferable formation of isomer **4**. Isomer **4** quantitatively forms in

Scheme 7



nonpolar media in the temperature range 10 – 30 °C at the NBD concentration > 3 mol litre^{-1}. Increasing reaction temperature along with decreasing NBD concentration lead to an increase in the content of *exo* – *trans* – *endo*-isomer **6**: at 100 °C and an NBD concentration of 0.5 mol litre^{-1}, its yield is as large as 95%. Varying these parameters makes it possible to obtain a required ratio between compounds **4** and **6** (Fig. 2).

In order to improve the feasibility of the NBD cyclodimerization process, heterogeneous catalysts have been proposed.[71] Unmodified acidic zeolite systems are, as a rule, nonselective in the formation of isomers retaining the norbornene structure. The catalysts obtained by the impregnation of silica gel with nickel salts and their subsequent high-temperature reduction with heavy paraffins show a rather high activity and selectivity to pentacyclic dimers.[72]

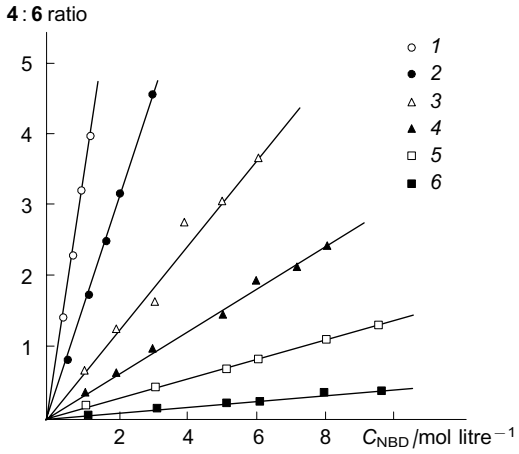


Figure 2. Ratio of dimers **4** and **6** as a function of norbornadiene concentration and temperature (solvent is n-nonane).[68]
T /°C: (*1*) 20, (*2*) 40, (*3*) 60, (*4*) 80, (*5*) 100, (*6*) 120.

3.3. Codimerization of norbornadiene with unsaturated compounds

Codimerization involving NBD is rather promising for synthesis of polycyclic compounds. It is an alternative

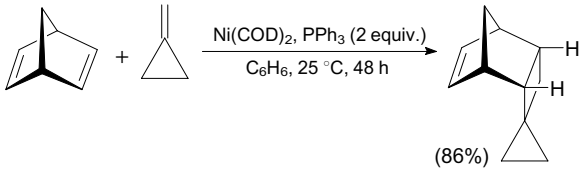
synthetic method to diene synthesis reactions involving CPD and sometimes more preferable.[2,5]

The range of substrates used in catalytic codimerization with NBD is rather limited. This is due to the peculiarities of the complexation of NBD and the second substrate on the metal atom. The comonomer should have a coordination capacity comparable to that of NBD in order to form a mixed heterosubstrate complex. Such properties are characteristic of alkenes with highly reactive double bonds, alkynes, and also some oxygen- and nitrogen-containing compounds. The codimerization of unsaturated compounds with NBD leads to [2π + 2π]- and [2π + 4π]-cycloaddition products, and both types can have geometric and optical isomers. The [2π + 2π]-cycloaddition products retain the norbornene endocyclic double bond and can be used for further transformations, for example, in metathesis oligomerization or polymerization. The codimerization products containing several double bonds of different reactivity are rather promising in synthesis of special rubbers.

Here, we address only those processes and catalysts that lead to norbornene derivatives with an endocyclic double bond.

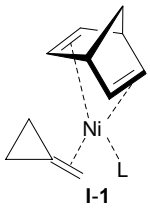
Alkenes with electron-withdrawing substituents usually react with NBD in the presence of Ni^0 catalysts to form [2π + 4π]-adducts.[73] However, stressed alkenes, such as methylenecyclopropane (MCP), react with NBD to give mainly *endo*-[2π + 2π]-cycloadducts (Scheme 8).[74]

Scheme 8



It is likely that such a spatial structure of the product largely depends on the combination of ligands in key intermediate **I-1**, in which NBD is coordinated to nickel as an *endo*-bidentate ligand.

Structure I-1



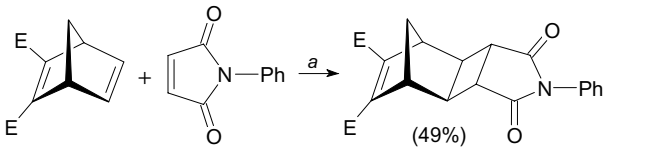
I-1

Attempts of enantioselective cycloaddition of NBD and MCP with the use of chiral phosphine ligands did not lead to positive results. When Ni^0 is replaced by Pd^0 as a catalyst, [3π + 2π]-cycloadducts are formed.[75]

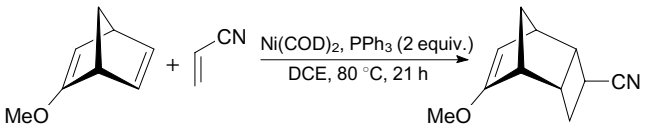
Despite the fact that substituted NBDs, as a rule, enter into [2π + 4π]-cycloaddition with alkenes having electron-withdrawing substituents, in some cases high regio- and even stereoselectivity is observed with respect to [2π + 2π]-cycloaddition. Such reactions proceed with the participation of the unsubstituted double bond of NBD, and the nature of the substituents in the 2- and 3-positions can affect the *exo*- or *endo*-direction of the addition.[31,33]

Electron-withdrawing substituents (E) promote *exo*-cycloaddition, while electron-donating substituents shift the reaction towards *endo*-adducts (Scheme 9).[76–78]

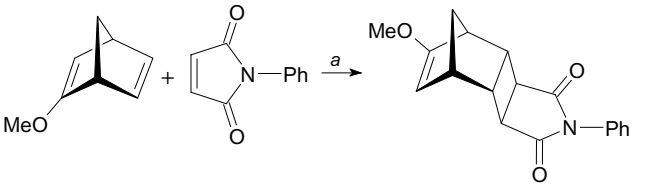
Scheme 9



(*a*) $Ni(COD)_2$, PPh_3 (2 equiv.), PhMe, 110 °C, 16 h



(52%; *endo* : *exo* = 4 : 1)



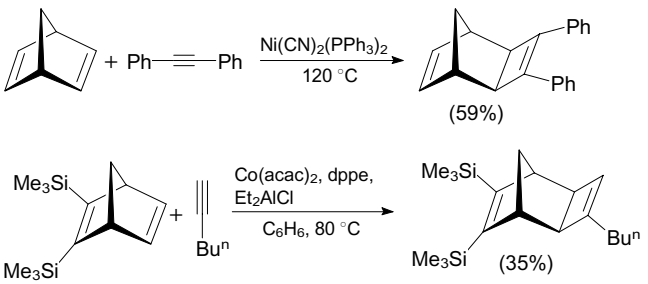
(*a*) $Ni(COD)_2$, P (2 equiv.), DCE, 80 °C, 21 h;
P = PPh_3 (69% yield, *endo* : *exo* = 5 : 1); $P(OPh)_3$ (34%, *endo* : *exo* = 12 : 1)

In the last reaction in Scheme 9, the replacement of a phosphine ligand by a phosphite one enhances the stereoselectivity toward the *endo*-isomer.[79]

Acetylenes give, as a rule, [2π + 4π]-adducts with NBD; however, there are some examples of the formation of [2π + 2π]-cycloaddition products.[80] Some iron and cobalt compounds also promote [2π + 2π]-addition in low yield, and the resulting adducts have exclusively an *exo*-structure (Scheme 10).

Low-valent ruthenium and rhodium complexes catalyse the [2π + 2π]-cycloaddition of NB and NBD with various acetylenes (Scheme 11).[81,82]

Scheme 10



Scheme 11

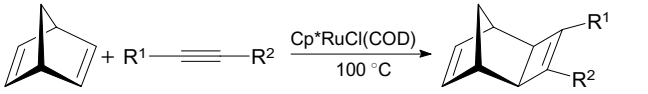


Table 3. Influence of the substituent nature in alkyne on the product yield (see Scheme 11).[81,82]

R^1	R^2	Time /h	Yield (%)
CO_2Me	CO_2Me	24	37
Me	CO_2Me	24	87
Ph	Ph	120	23

The nature of substituents essentially affects the reaction rate (Table 3).

Variants of NBD reactions with alkynes catalyzed by cobalt compounds are known; these reactions involve the insertion of carbon monoxide[83,84] or azomethines.[85]

It is worth noting that the products of $[2\pi + 2\pi]$-cycloaddition of NBD to alkenes are mainly *endo*-adducts, while the reactions with acetylenes give only *exo* products. The two-phase hydroformylation reaction of NBD involving one or two double bonds has been described.[86]

Under mild conditions, the arylboronation of NBD[87] and the addition of thioethers to it[88] catalyzed by palladium complexes proceed stereoselectively. The reaction products have an *exo*-structure. In the presence of palladium complexes, the cross-coupling of NBD with aryl halides occurs with high stereoselectivity in 95% yield (the Mizoroki – Heck reaction).[89]

Codimerization processes involving NBD have a number of qualitative analogies: the intramolecular character of formation of a codimer implies the formation of heteroleptic π-complexes, and the substrate should have the coordination ability intermediate between those of mono- and bidentate NBD molecules.[22] Knowledge of these features is necessary for synthesis of individual products with high technological characteristics.

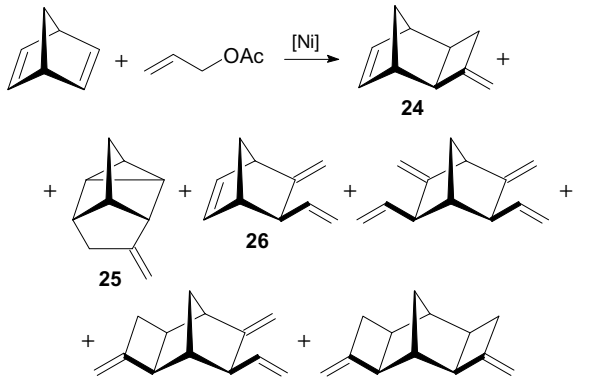
Metal complex catalysts are mainly used in preparative syntheses, and their regeneration is laborious and ineffective. The heterogeneous catalytic variant of carrying out the mentioned reactions is undoubtedly more industrially feasible; however, there are very few such studies involving NBD.

A heterogeneous catalyst of the [2 + 2]-codimerization of NBD with methyl vinyl ketone (MVK) has been developed. The catalyst is formed upon the high-temperature reduction of nickel chloride preliminarily applied to alumina with $C_{16}-C_{18}$ paraffins.[73] Depending on reaction conditions (temperature, reactant ratio, the presence of a solvent), the catalyst thus obtained is able to selectively catalyze [2 + 2]-cycloaddition processes: NBD cyclodimerization, MVK dimerization and codimerization of NBD with MVK.

3.4. Catalytic allylation of norbornadiene

The catalytic allylation of a stressed double bond in NB was described for the first time in 1979 by Catellani *et al.*[90] This promising synthesis of structurally unique NBD-based compounds has been later further developed.[91–98] The reaction makes it possible to synthesize, in one technological stage, different NB derivatives that have two (or more) double bonds with different reactivity. The sources of allyl fragments are organic esters. The uniqueness of the reaction is in the character of addition of the allyl fragment: it is cyclic or with C – C bond cleavage rather than traditional linear addition (Scheme 12).

Scheme 12



The catalytic system $Ni(acac)_2-AlEt_3-P(OR)_3$ is rather active and sufficiently selective in synthesis of *exo*-methylenecyclobutane derivatives.[91,92] A system generated *in situ* from $Ni(All)_2$ in the presence of tertiary phosphites is also promising.[93–97] The structure of the allylating agent — allyl ester — has no decisive significance. In particular, not only allyl acetate (AA) but also allyl propionate and allyl benzoate can be used.[93] When allyl formate (AF) is used, high reactant conversions are not achieved because of the decomposition of the nickel – phosphite catalytic system. The isomeric composition of the products depends on temperature and nickel : phospite molar ratio.

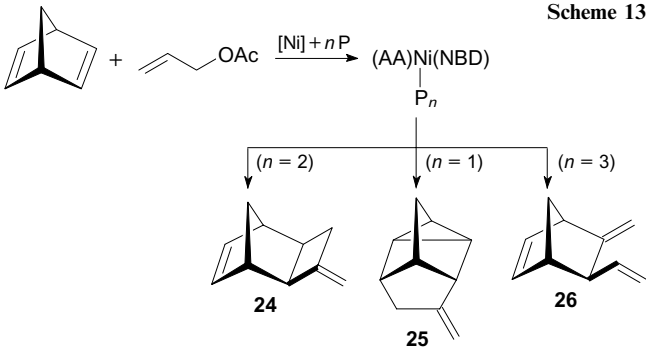
The catalytic allylation of NBD and NB derivatives is a complex multiparameter and nonstationary process.[95,96] Detailed study of kinetics and mechanism in the presence of the $Ni(All)_2-n\,P(OPr^i)_3$ catalytic system with the use of a combination of physicochemical methods demonstrates the existence of equilibrium stages, which can be described by Eqn (3).

$$NiP_n \rightleftharpoons NiP_{n-1} + P \qquad (3)$$

Complexes with a different number of phosphite ligands have been detected by ^{31}P NMR in model systems and under catalytic reaction conditions.

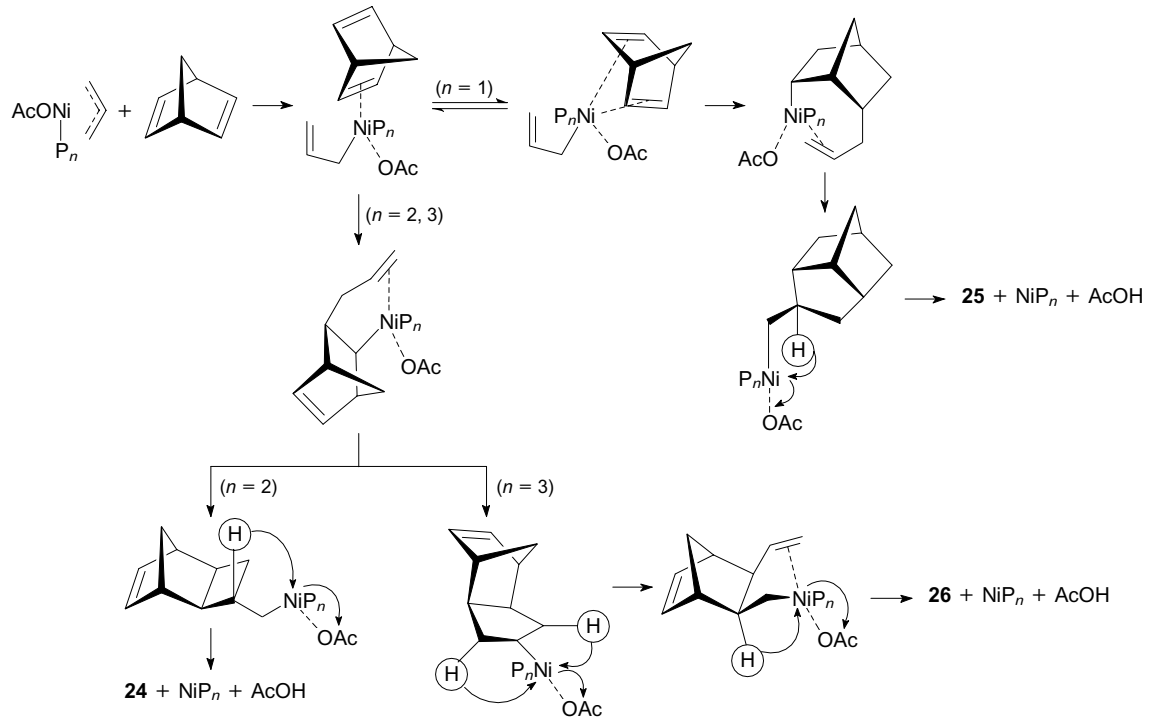
It follows from kinetic data that the formation of individual products **24** – **26** is determined by the presence of nickel complexes with a different number of phosphite ligands in the catalytic system (Scheme 13).

Scheme 13

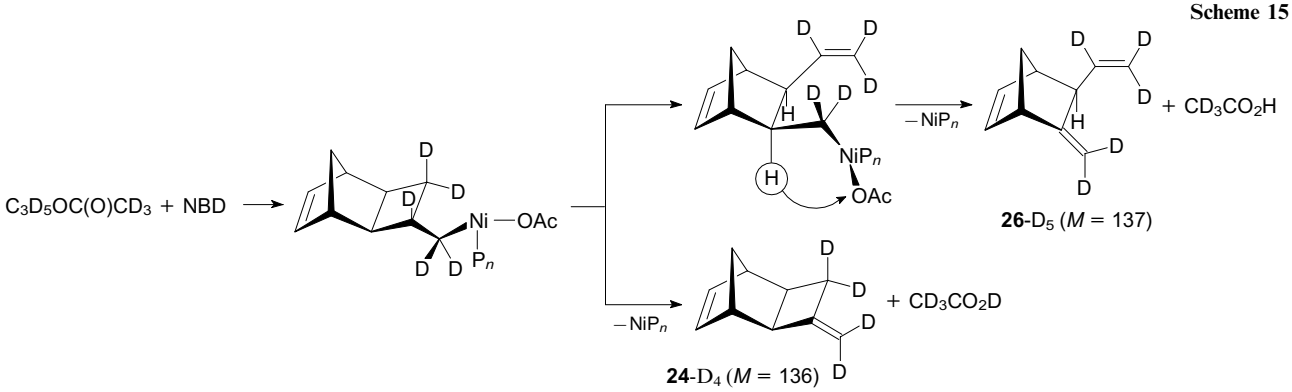


A mechanism of catalytic allylation of NBD (Scheme 14) has been suggested,[96] according to which the $AllNiP_nOAc$ complexes dominate in the reaction mixture. The NBD molecule, being coordinated to the nickel atom,

Scheme 14



Scheme 15



promotes the $\eta^3-\eta^1$-isomerization of the allyl ligand and then is inserted into the η^1-allyl–metal bond. Then, depending on the *n* value, different routes of cyclization are realized, which are completed with β-hydride transfer, formation of the products and NiP_n regeneration.

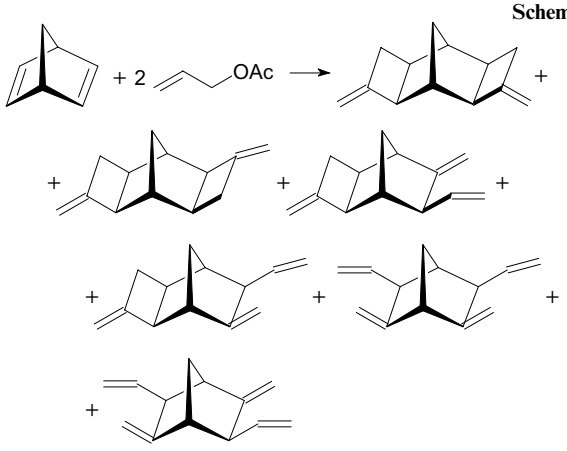
The hydride transfer step is evidently rate-limiting. For the model system $C_3D_5OC(O)CD_3$–NBD, it has been demonstrated that this step involves the β carbon atom. The weights of products **24** and **26** are different, which confirms the possibility of elimination of the hydrogen atom from the β-position of both the NBD ring and the allyl moiety (Scheme 15).[96]

Acetic acid that forms in the course of reaction destabilizes the catalytic system. This is why the TON in a static reactor, as a rule, does not exceed 150 – 200. The use of zeolites selectively absorbing acetic acid makes it possible to increase the TON to 2000.[95]

The use of these features allows one to obtain individual products in 85% – 95% yield by varying reaction conditions.

The process with the use of the twofold allyl acetate excess with respect to NBD is of considerable interest. The second allylation of compounds **24** and **26** with norbornene

Scheme 16

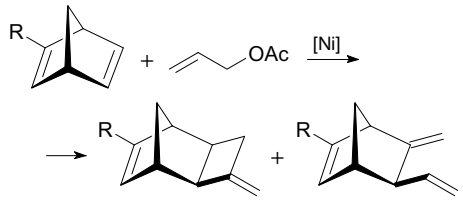


structures leads to a large number of isomeric products (Scheme 16).[96]

The structure and ratio of the NBD double allylation products depends on conditions — temperature and P : Ni ratio. The allylation rate of the first double bond in NBD is several times as large as the rate of the second step.

Cooligomerization catalysts are slightly sensitive to the structure of substituents in the 7-position of the NBD molecule.[94, 95] At the same time, the presence of a substituent at the double bond (R = OMe) in NBD suppresses the allylation reaction at the substituted double bond. Variation of the phosphite : nickel molar ratio and temperature makes it possible to obtain individual products in 80% – 95% yields (Scheme 17).

Scheme 17



For a long time, the catalytic allylation reactions of NB and NBD were realized only in the presence of nickel complexes stabilized with phosphite ligands. Although the possible participation of other metals (Fe, Co, Rh, Pd, Pt) as catalysts for this reaction was previously predicted, no relevant information has been reported. These assumptions were based on a large-scale study of the stoichiometric interaction of a number of homoleptic allyl complexes of transition metals with NBD.[97] Only in 2000 did the first examples of the use of palladium complexes appear,[98] which have been substantially developed in a series of subsequent studies.[99 – 101]

Palladium phosphine complexes catalyze the NBD allylation reaction analogously to the nickel complexes. As a rule, they are less selective with respect to the formation of individual products, except the case when the reaction is carried out in an ionic liquid medium and palladium clusters $Pd_{147}(phen)_{32}O_{60}(OC(O)Bu^t)_{30}$ (phen is 1,10-phenanthroline) act as catalysts.[102] A significant circumstance in the case of Pd catalysts is the possibility of carrying out the reaction in the presence of oxygen, while for Ni-systems this is absolutely unacceptable. Nevertheless, the catalytic activity of nickel catalysts significantly exceeds that for palladium ones.

An original result was obtained using palladium acetate $Pd_3(OAc)_6$ as a catalyst precursor and AF as an allylating agent. It was mentioned above that AF cannot be considered as the optimal allylating agent in nickel-catalyzed reactions due to the rapid deactivation of the catalytic system. The palladium-catalyzed reaction of AF and NBD in the absence of phosphine ligands leads to the only product, 5-allylnorbornene, in 95% – 98% yield at high catalyst activity and stability.[103] The mechanism of this reaction, including that with the use of AF-D_6 has been studied in detail.

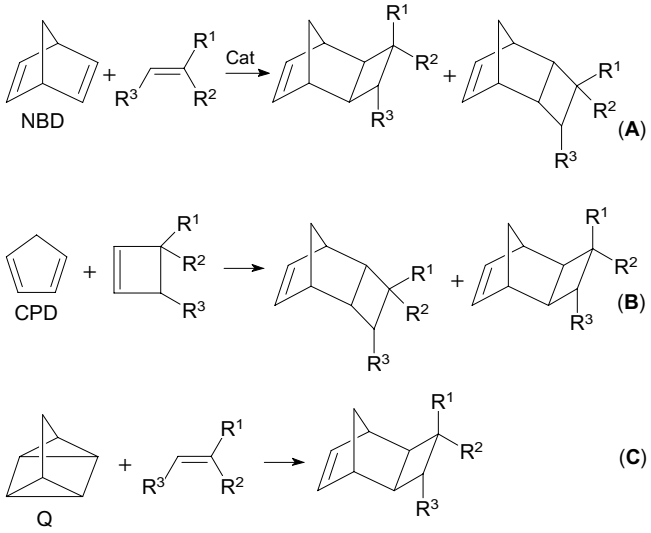
Despite the fact that the overwhelming number of studies on NBD deal with the use of homogeneous catalytic systems, there are some examples of the use of heterogeneous catalysts in NBD allylation reactions. In particular, bis(allyl)nickel (2 mass %) supported on silica gel exhibits high activity and selectivity with respect to products **24** and **26** with a norbornene structure.[104] Based on the regularities of the Pd-catalyzed homogeneous reaction, heterogeneous catalysts have been developed, which consist of $Pd_3(OAc)_6$ (1%) supported by γ-alumina or immobilized on KSKG silica gel.[105] The catalysts exhibit moderate activity and high selectivity with respect to 5-allylnorbornene.

Thus, the allylation reaction of NBD and NB derivatives is of general nature and can act as a promising method of synthesis of unavailable polycyclic monomers.

3.5. Synthesis of new monomers through [2 + 2 + 2]-cycloaddition of alkenes to quadricyclane

Norbornene and its derivatives are highly reactive due to the high strain of the norbornene skeleton and the accessibility of a double bond for interaction with catalysts and reagents. Chemically, this resulted in the unique ability of compounds of this series to polymerize by various mechanisms to form products with different structures and valuable physicochemical properties (see below Scheme 29 in Section 4.1). However, the presence of bulky or functionalized substituents in the norbornene molecules hinders or even completely blocks the polymerization. A technique that makes it possible to restore the ability of such derivatives to efficiently polymerize is a shift of blocking substituents by some distance from the double bond. This shift can be accomplished through the synthesis of tricyclononenes (TCN) — norbornene derivatives with a fused four-membered ring.[7, 12, 106] TCN (tricyclo[4.2.1.$0^{2,5}$]nonene) has a large amount of energy, which stimulates its high reactivity. The following briefly summarizes the methods for the synthesis of TCN and its derivatives, which include three main approaches (**A**, **B** and **C**) reflected in Scheme 18.

Scheme 18

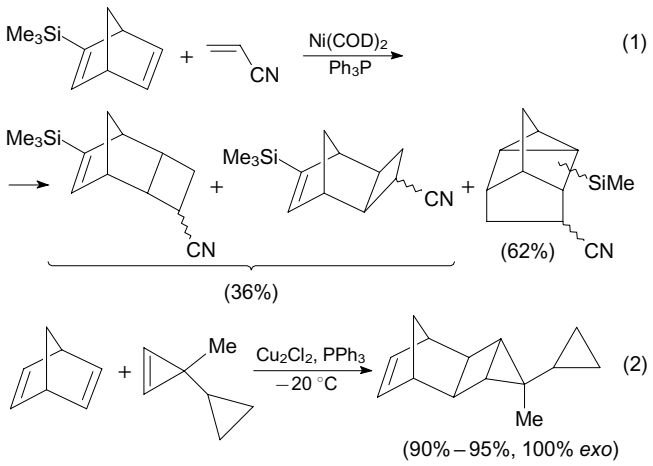


One possible method to synthesize TCN is the catalytic addition of various alkenes to norbornadiene (Scheme 18, method **A**). Schematically, these processes have been already mentioned in section 3.3 of this review. In the case of strained methylenecyclopropane, norbornadiene undergoes the catalytic cycloaddition reaction in the presence of a nickel complex to form a mixture of *exo*/*endo*-isomers (see Scheme 8); in addition, the products contain minor

amounts of deltacyclane (tetracyclo[2.2.1.$2^{3,5}$.$0^{2,6}$]nonane) and dimers of the starting compounds. The composition of the final mixture essentially depends on the reaction conditions.[74, 107]

Norbornadiene derivatives with bulky substituents (for example, trimethylsilylnorbornadiene) also enter into the Ni complex-catalyzed [for example, $Ni(COD)_2 - Ph_3P$] [$2\pi + 2\pi$]-cycloaddition reaction with very reactive dienophiles, for example, with acrylonitrile [Scheme 19, reaction (1)].[108] In this case, cycloaddition occurs on the less sterically hindered side.

Scheme 19

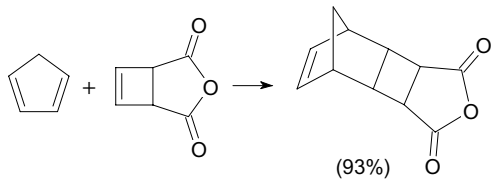


To accomplish a regio- and stereospecific NBD reactions with various alkenes, a search for new catalysts is required, since the methods described in the literature imply NBD reactions only with alkynes (see Section 3.3) or with strained alkenes [see Scheme 19, reaction (2)].[108 – 115] It should be noted that this reaction can only be used when dealing with micro amounts of reactants due to the difficulty of obtaining the initial strained alkenes and large loads (5 mol.%) of poorly accessible Ru catalyst in the reaction with alkynes.

The catalytic [$2\pi + 2\pi$]-cycloaddition of alkenes/alkynes to NBD gives a mixture of *exo*- and *endo*-isomers. In addition to their formation, a side [2 + 2 + 2]-cycloaddition reaction is observed leading to deltacyclane derivatives.

Yet another method of synthesis of TCN is based on the Diels – Alder reaction of cyclopentadiene with cyclobutene derivatives (see Scheme 18, method **B**). As a rule, the reaction mainly gives the *endo*-isomer. In particular, the reaction of 3-cyclobutene-1,2-dicarboxylic anhydride with cyclopentadiene in boiling benzene leads stereospecifically to the formation of the *endo*-isomer with a small amount of the *exo*-cycloadduct (Scheme 20), which was proved by NMR.[116]

Scheme 20



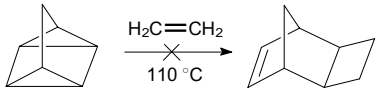
However, this method of tricyclononene synthesis is unsuitable because of the poor availability of the starting cyclobutenes.

The most attractive method seems to be the synthesis of tricyclo[4.2.1.$0^{2,5}$]non-7-ene and tricyclo[4.2.1.$0^{2,5}$]nona-3,7-diene through the thermal [$2\sigma + 2\sigma + 2\pi$]-cycloaddition of tetracyclo[3.2.0.$0^{2,7}0^{4,6}$]heptane (quadricyclane, Q), which has a high amount of energy (78.7 kcal mol^{-1}), to substituted alkenes or alkynes (see Scheme 18, method **C**).[117] Quadricyclane is extremely reactive due to its strained cyclic structure. In addition, it is stable and readily produced through photochemical isomerization of NBD (see Scheme 6), which makes it a suitable reagent in organic chemistry, in particular, for synthesis of TCN.[117]

Quadricyclane enters into the condensation reaction with alkenes and alkynes; the reaction proceeds mainly stereo- and regiospecifically to give only the *exo*-isomer.[117] The norbornene *exo*-derivatives are known to be more reactive in polymerization reactions as compared with the *endo*-isomers,[118, 119] which makes this method even more attractive for TCN synthesis.

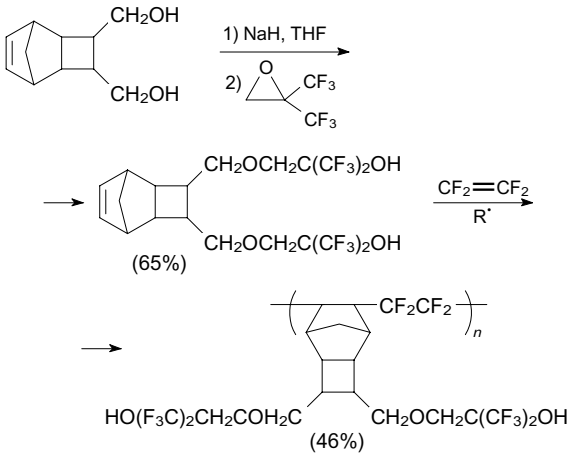
It is worth noting that Q does not condense with non-activated alkenes and alkynes. For example, it does not react with unsubstituted ethylene even in the course of long heating (110 °C) (Scheme 21).[120]

Scheme 21



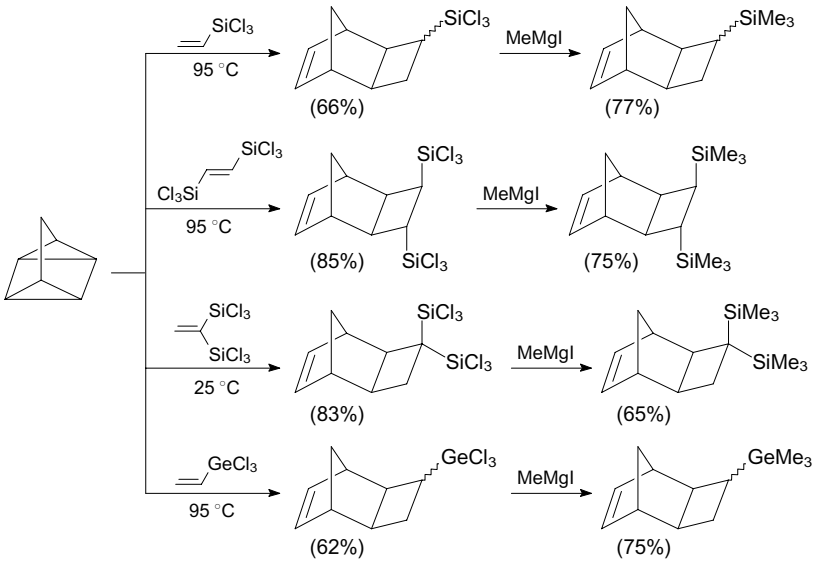
Alkenes containing electron-withdrawing substituents (CN, CO_2R, fluorine-containing groups, *etc.*) are subjected to cycloaddition to quadricyclane by analogy with the Diels – Alder reaction.[106, 117, 120, 121] The presence of these substituents made it possible to synthesize tricyclononene derivatives whose addition polymers and copolymers exhibited properties of high-performance photoresists transparent at a wavelength of 157 nm (Scheme 22).[106, 122, 123]

Scheme 22



As a rule, attempts to polymerize norbornene analogues containing the required number of these substituents were unsuccessful or led to low-molecular-weight polymers in low yield.

Scheme 23



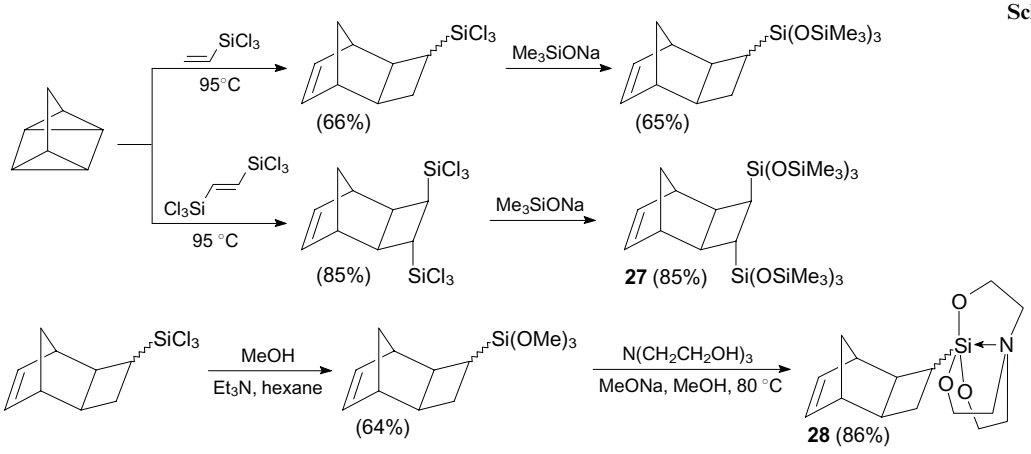
Recent studies focusing on qualified application of tricyclononenes resulted in synthesis of polymers capable of separating gases. It turned out that chlorosilyl groups can act as electron-withdrawing substituents in alkenes. From 2009 to 2017, researchers at the Insitute of Petrochemical Synthesis, RAS, have published a series of studies dealing with thermal $[2\sigma+2\sigma+2\pi]$-cycloaddition of alkenes containing Si–Cl bonds to quadricyclane to give *exo*-chlorosilyltricyclononenes.[7,12] The latter were methylated (or alkoxy/silyloxylated) to give monomers that polymerized to produce materials for efficient gas-separation membranes.[7,12] Chlorosilylalkynes and analogous germanium derivatives reacted with quadricyclane in a similar way. The condensation reactions with unsaturated chlorosilanes and chlorogermanes proceeded at 22–95 °C depending on the number and arrangement of electron-withdrawing groups (Scheme 23).[124–127]

A detailed study of this reaction, new for organometallic chemistry, was undertaken to determine the range of active alkenes containing Si, Ge and Sn atoms in the substituents, as well as to evaluate the relative activity of alkenes and synthesize new monomers with different regularly changing structure and spatial arrangement of substituents.[126,127] Tin-containing substituents ($SnCl_3$) led to the isomerization of quadricyclane to norbornadiene. The course of the thermal condensation of Q with $SiCl_3$-substituted alkenes and alkynes was monitored by NMR to elucidate their transformation in time. Based on the data obtained, silicon-substituted alkenes and alkynes were arranged in a series according to their activity in the above condensation $Cl_3SiC{\equiv}CSiCl_3 > Cl_3SiCH{=}CHSiCl_3 > Cl_3SiC{\equiv}CH > Cl_3SiCH{=}CH_2$.[125–128]

Structural features of TCN make it possible to synthesize monomers crowded with bulky substituents, polymerize them up to high-molecular-weight products and study the gas permeability of the produced polymer films. As a rule, similar operations are impossible for related norbornene derivatives.[7,12,106] Scheme 24 shows the synthesis of TCN **27** with six trimethylsilyloxy groups and silatranyltricyclononene **28**, and Fig. 3 shows their structures (according to single-crystal X-ray diffraction), which demonstrate the *exo*-position of the four-membered ring.[126–131]

These results confirm the efficiency of displacement of substituents at a greater distance from the norbornene double bond to enhance its reactivity. Implementation of this approach through $[2+2+2]$-cycloaddition of alkenylchlorosilanes to quaricyclane affords *exo*-structures without impurity of *endo*-isomers, which additionally provides the

Scheme 24



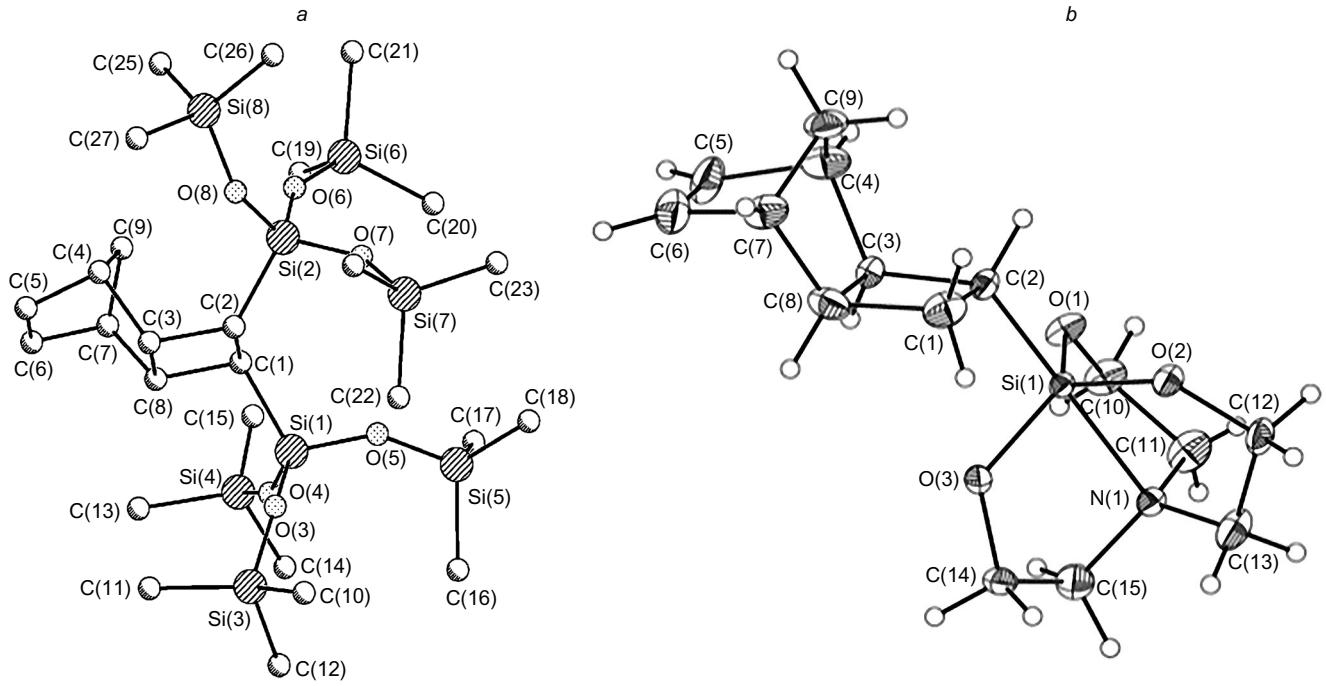
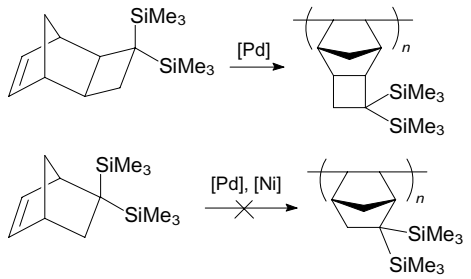


Figure 3. Structure of tricyclononene **27** (*a*) [130] and silatrane derivative **28** (*b*) [131] according to single crystal X-ray diffraction.

formation of monomers with required substituents and significantly facilitates their polymerization.

In particular, norbornene containing two Me_3Si groups was unable to polymerize by the addition scheme (Scheme 25). At the same time, geminal and vicinal *exo*-bis(trimethylsilyl)tricyclononenes polymerized to high-molecular-weight products, which exhibited outstanding gas-separation characteristics (see Scheme 25).[121, 125, 132 – 134]

Scheme 25



The behaviour of ethylene derivatives with three silicon-containing groups with a different ratio of the Si—Cl and Si—Me bonds in [2 + 2 + 2]-cycloaddition to quadricyclane has been studied (Fig. 4).[46, 121, 135]

Alkenes **I** – **IX** react with Q, while alkene **X**, containing weak electron-withdrawing $SiMe_2Cl$ groups, does not react. Compounds **I** – **III**, **V**, and **VI** react with Q at room temperature, while alkenes **IV** and **VII** – **IX** react only on heating (95 °C). The reaction is monitored by ^1H NMR, since the signals of the starting compounds, reaction products and norbornadiene by-product in the range of olefin protons are well resolved. Alkene **I**, containing three strong electron-withdrawing $SiCl_3$ groups, is the most reactive one. Gradual

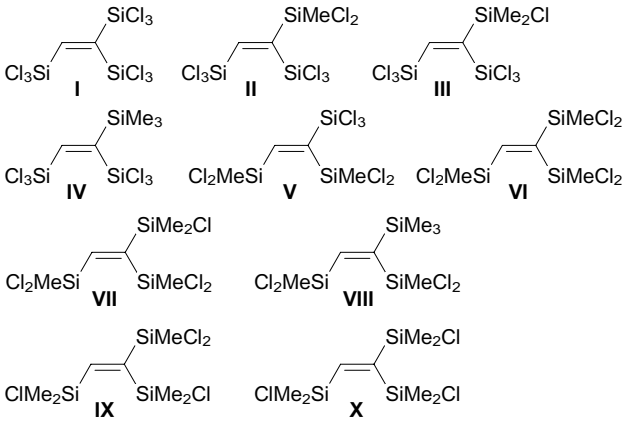


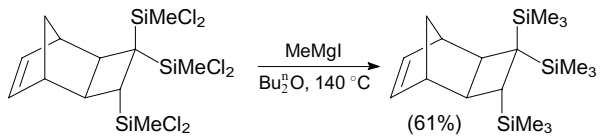
Figure 4. Some alkenes studied in the [2 + 2 + 2]-cycloaddition to quadricyclane.[46, 121, 135]

increase in the number of methyl groups at silicon atoms in substrates lead to a decrease in their activity. In addition, the alkene activity also depends on the position of methyl groups at silicon atoms. For example, alkene **V**, containing two Me groups at different silicon atoms, is more active than alkene **III**, in which methyl groups are located at the same silicon atom. The difference between the activities of these substrates is presumably associated with double bond polarization. It is likely that the double bond in alkene **V** is more polarized than in alkene **III**; the same is valid for alkenes **IV** and **VI**. This is indirectly confirmed by ^{13}C NMR data on the difference between the chemicsal shifts of the carbon atoms at the double bond.[121] It is worth noting that 1,2-bis(trichlorosilyl)ethylene is more active

than alkene **IV**, while vinyltrichlorosilane is less active than alkenes **I** – **IV** and **VI**.[121]

Exhaustive methylation of the adduct synthesized by condensation of alkene **VI** with quadricyclane by the Grignard reagent under severe conditions led to the formation of tricyclononene containing three bulky $SiMe_3$ groups in good yield without formation of by-products (Scheme 26).[121]

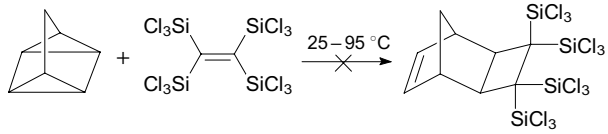
Scheme 26



The data obtained make it possible to determine the range of chlorosilylethylenes active in the $[2\sigma + 2\sigma + 2\pi]$-cycloaddition to Q and elucidate the factors that affect the alkene activity in this reaction.

Since the activity of alkenylchlorosilanes in the condensation reaction with Q increases with an increase in the number of electron-withdrawing $SiCl_3$ groups from vinyltrichlorosilane to 1,1,2-tris(trichlorosilyl)ethylene, a further increase in the alkene activity with an increase in the number of electron-withdrawing $SiCl_3$ groups to four might be expected. However, it unexpectedly turned out that tetrakis(trichlorosilyl)ethylene did not react with Q both at room temperature and on heating to 95 °C (Scheme 27).[121]

Scheme 27

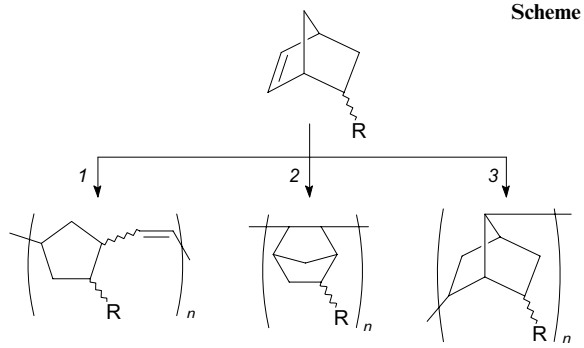


The reasons for such a behaviour can be both the low double bond polarization and steric hindrances generated by bulky substituents ($SiCl_3$) for the attack of tetrakis(trichlorosilyl)ethylene at quadricyclane molecules. According to quantum chemical DFT calculations, the energy barrier of the $[2\sigma + 2\sigma + 2\pi]$-cycloaddition of chlorosilylethylenes to Q decreases with an increase in the number of $SiCl_3$ groups. The lowest activation barrier was obtained for tris(trichlorosilyly)ethylene, which was most active in this reaction. A further increase in the number of $SiCl_3$ groups to four led to the more than twofold increase in the energy barrier (from 15.8 to 33.4 kcal mol^{-1}). It turned out to be even higher than that for unsubstituted ethylene (29.8 kcal mol^{-1}) (Refs 121, 135). It is likely that large steric hindrance generated by four $SiCl_3$ groups is responsible for the inactivity of tetrakis(trichlorosilyl)ethylene in the reaction with quadricyclane.

4. Polynorbornenes

Norbornene and its derivatives are widely used in synthesis of different polymer materials. This is caused by the ease of their synthesis and their unique ability to polymerize by different mechanisms to form products with a number of practically valuable properties. Norbornene actively polymerize by the (*1*) ring-opening metathesis, (*2*) addition (vinyl) and (*3*) isomerization polymerization schemes (Scheme 28).

Scheme 28



The first two ways are realized under metal complex catalysis conditions being catalyzed by transition metal compounds. Isomerization polymerization/oligomerization is a poorly studied process. It has been detected with radical and cation initiation and is beyond the scope of this review. The number of works addressing the polymezation of norbornenes and published in recent years is extremely large. This section basically focuses on main advances and current trends that have been developed during the past 3 – 5 years.

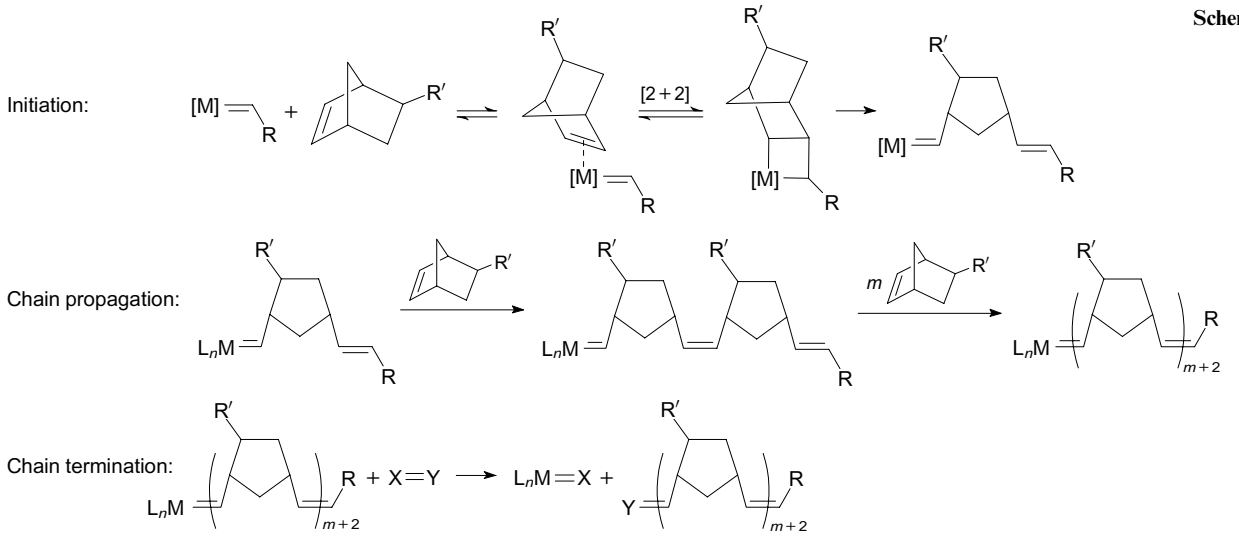
4.1. Ring-opening metathesis polymerization of norbornenes

In our opinion, significant progress has been achieved, first of all, in ring-opening metathesis polymerization (ROMP). For norbornene, the ROMP was first revealed in 1955. Since that, progress in the development of efficient catalytic systems and studies of mechanisms and applications of olefin metathesis (OM) reaction have contributed to the transformation of this reaction to a powerful tool of organic and polymer synthesis.[136, 137] Key features of the ROMP of norbornene and its derivatives have been comprehensively described in the book by Ivin and Mol,[136] handworks edited by Grubbs [137, 138] and in reviews.[139 – 145]

Polymerization metathesis of norbornene is a thermodynamically favourable process that involves the cleavage of the endocyclic double bond in the strained bicyclic skeleton; as a result, the reaction is fast and irreversible. This made norbornenes to be among the most popular substrates in ROMP. The reaction proceeds by a chain mechanism involving metal carbenes (Scheme 29). The reaction is initiated by a metal carbene complex, which is coordinated to norbornene and forms a metallacyclobutane intermediate as a result of the [2 + 2]-cycloaddition. The latter decomposes to give a new metal carbene complex responsible for chain propagation. The chain termination is accomplished by adding the reagent that forms an inactive metal carbene.

Considerable recent advances in the ROMP of norbornenes have been made due the development of efficient catalysts — metal carbene complexes of Mo, Ru, W, Re *etc.*[136 – 138] For the synthesis of new catalysts and discovery of the carbene mechanism of metathesis, R.Schrock, R.Grubbs and Y.Chauvin were awarded theNobel Prize in chemistry in 2005.[146, 147] Among the basic advantages of single-component metal alkylidene catalysts, in addition to their stability, high activity and tolerance to functional

Scheme 29



[M] is a metal atom with its ligand environment

groups, are their capability to perform living polymerization of cycloalkenes, as well as the possibility to monitor the reaction active sites by spectral methods.

Since that time, a burgeoning growth of the number of publications dealing with the development of efficient metal carbene complex catalysts of metathesis reaction began. The literature presents data on the synthesis of hundreds of catalysts like Schrock Mo and W carbene complexes and Grubbs Ru carbene complexes with various ligands: symmetric and asymmetric four-, five- and six-membered N-heterocyclic carbenes (NHCs), chiral mono- and bidentate NHCs *etc*.[145] These catalysts are able to initiate asymmetric metathesis reactions of functionalized alkenes, operate in aqueous and protonic solvents and be active only under external impact.[137, 138, 143, 148] The last circumstance is especially important for industrial polymerization of highly active monomers, such as dicyclopentadiene (DCPD). To this end, a lot of so-called latent catalysts have been synthesized; as a rule, they have a chelated or sterically protected metal site and become active only on heating.[149 – 151] Catalysts activated by acids, mechanical impact, chemical or electrochemical oxidation and photo irradiation[143] are known; the metal-free photoactivation of ROMP has also been reported.[152]

Among the latest achievements, the synthesis of *cis*- and *trans*-selective catalysts is worth noting. This is a serious success in OM, since earlier attempts to accomplish stereoselective metathesis failed, which limited its use in synthesis of biologically active compounds most of which contain *cis* double bonds. For polymers, stereoselective synthesis can afford a polymeric chain of single structure, *i.e.*, a sterically ordered chain of definite tacticity. Polynorbornenes and polynorbornadienes synthesized through the ROMP reaction contain double bonds located near the tertiary chiral carbon atoms. When ROMP involves unsubstituted or symmetrically substituted norbornenes and norbornadienes, four isomeric positions of two neighbouring monomer units in dyads are hypothetically possible (Fig. 5).

In 1993, Schrock and co-workers[153] synthesized molybdenum imidoalkylidene complexes containing achiral biphenolate (Biphen, Fig. 6 *a*) or binaphtholate ligand and used them in synthesis of *cis*-isotactic poly[2,3-bis(methoxycarbonyl)norbornadiene] and analogous polymers. The *cis*-isotactic structure forms as a result of enantiomorphic control provided by a chiral biphenolate initiator. This

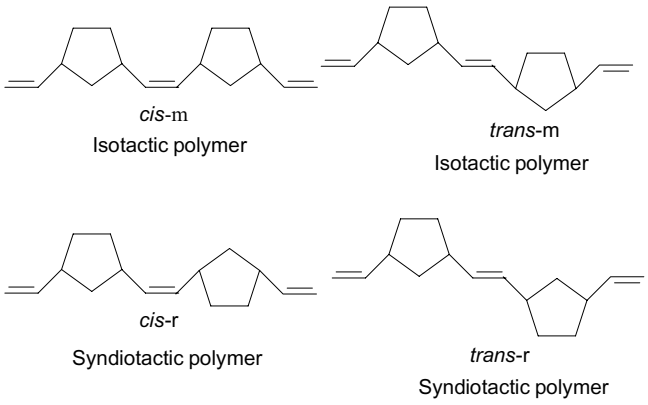


Figure 5. Isomeric positions of neighbouring monomeric units in the polynorbornene chain.[136]
r is *rac*, m is *meso*.

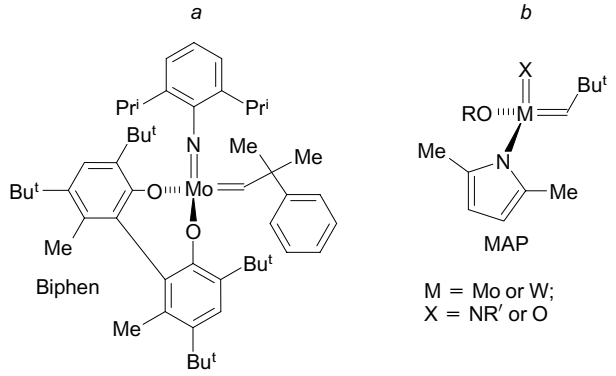


Figure 6. Stereoselective Schrock catalysts.[154]
Examples of a complex with biphenolate ligand (Biphen) (*a*) and monoaryloxide pyrrolide (MAP) complexes (*b*).

means that the monomer directed by a chiral (racemic) biphenolate approaches the M=C double bond only from one side after each insertion to give the next alkylidene. Thus, exclusively one stereostructure of a polymeric chain, isotactic, is formed. Further progress in synthesis of stereoselective Schrock Mo and W catalysts has been described in detail.[154 – 157] It has been recently found that Mo and W monoaryloxide pyrrolide (MAP) and other carbene complexes, analogous to those shown in Fig. 6 *b*, make it possible to synthesize *cis*-syndiotactic polynorbornenes and substituted polynorbornadienes.[158 – 160] This occurs through the attachment of the monomer on one side of the M=C bond at the first step and further attachment on the other side of the M=C bond at the next step. Such a stereogenic metal centre control is a result of that the stereogenic metal centre configuration is transformed (switched) at each polymerization step.

Recently, interesting results on the synthesis of V carbene catalysts have been obtained.[161, 162] In the presence of PMe_3, the V alkylidene complex $V(CHSiMe_3)(=NC_6H_3X_2\text{-}2,6)[OC(CF_3)_3](PMe_3)_2$ (X = H, Cl) catalyzes living and *cis*-selective polymerization of norbornene. With increasing temperature from 50 to 80 °C, the catalyst activity increases without loss of *cis*-selectivity, which is 98%.

In recent years, Ru carbene complexes exhibiting *cis*-selectivity in OM have been synthesized.[163, 164] The stereoselective *cis*-ROMP of norbornene occurs on Ru catalysts with the dithiolate ligand synthesized by Hoveyda and coworkers.[165] (Fig. 7). They afford *cis*-selectivity >98% in many cases and the TON up to 43 000; they are tolerant to alcohols. Interesting studies dealing with *trans*-selective metathesis have been started for small molecules.[164]

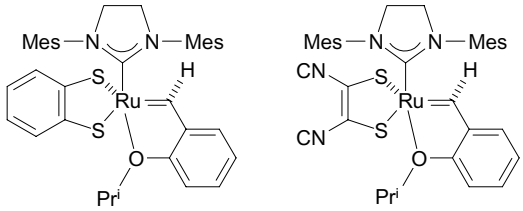


Figure 7. *cis*-Selective Ru catalysts with a dithiolate ligand in ROMP.[165]

Currently, several companies produce and sell various metathesis catalysts: Strem Chemicals, Inc.; Materia; Umicor; Evonik; Cazin; Zannan; Omega Cat System; Apeiron. Latent thermostimulated Ru catalysts have been developed in Russia.[166, 167] For the ROMP of norbornenes, commercially available catalysts are mainly used; some of them are shown in Fig. 8. Catalysts with NHC ligands (Grubbs catalyst of the second and third generation Gr-2 and Gr-3, Grubbs – Hoveyda catalyst of the second generation Gr-H-2, *etc.*) are more active.

An important issue is the catalyst stability in air and at elevated temperatures; therefore, studies are performed dealing with decomposition paths of catalysts and key factors promoting their decomposition, for example, formation of unstable methylidene complexes in the course of reaction, deactivation under the action of an electron-rich

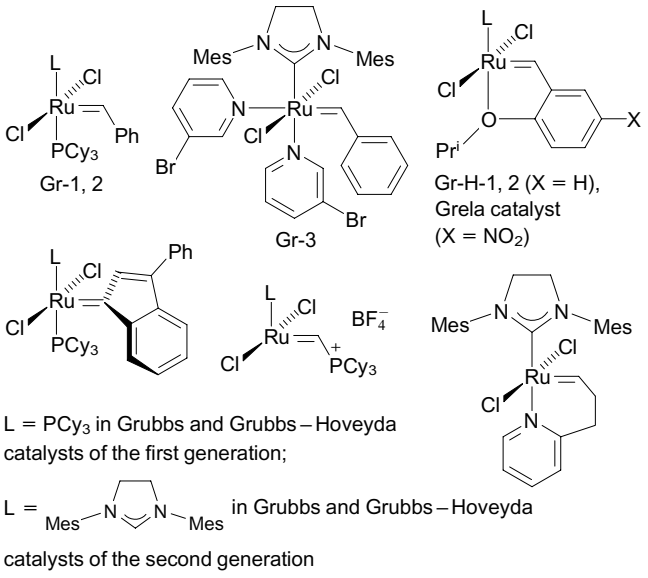


Figure 8. Olefin metathesis Ru-carbene catalysts.[145, 148]

substrate π-acids (for example, CO), under the action of alcohols, *etc.*[140]

The ways to remove the products of catalyst transformation from reaction mixtures after the end of OM reaction are being investigated. This is especially important in synthesis of pharmaceuticals, polymeric materials for electronics and high technologies. The most general strategy used for solving such problems implies modification of a catalyst by supporting it to solid materials (for example, silica gel or polymers, Fig. 9)[168] or by introducing, into the catalyst molecule, functional groups of ionic liquids, perfluorinated fragments and so on, which are subsequently removed form OM reaction mixtures by filtration, extraction and other methods.[169 – 171] Among the latest achievements, noteworthy is the supported acenaphthoimidazolylidene NHC carbene Ru complex, which demonstrates high activity during eight cycles.[172]

Thus, currently there is a tremendous assortment of metathesis catalysts. Nevertheless, there is no perfect cata-

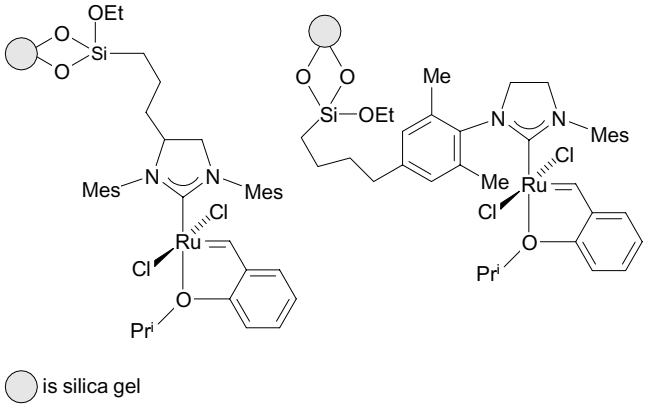


Figure 9. Silica-supported Grubbs – Hoveyda catalysts of the second generation.[168]

lyst. Depending on the task (preparative or commercial synthesis) and substrate type (linear alkenes, cycloalkenes, compounds with bulky functional groups, *etc.*), an optimal catalyst for the process can be selected. These can be both cheap and available classical systems and well-defined metal carbene complexes.

In addition to the catalyst, the ROMP activity is determined by the monomer structure. Unsubstituted norbornene is actually the most active monomer in ROMP, competing presumably only with cyclobutene. The position of the substituent in the norbornene molecule essentially affects its activity in polymerization. For methyl- and trimethylsilyl-substituted norbornenes and DCPD, it has been shown that *exo*-isomers are much more active than *endo*-isomers.[173 – 175] The introduction of a substituent into the 7-*syn*-position also significantly deteriorates the norbornene activity, hindering the coordination of the double bond to the catalyst in the course of ROMP. Polar groups are able to coordinate to the catalyst, thus decreasing its activity, which has been demonstrated when studying the kinetics of the ROMP reaction of norbornenedicarboxylates catalyzed by an N-chelated Grubbs – Hoveyda catalyst of the second generation.[176] A significant role is played by the distance between the substituent and the double bond. For example, in the presence of a Gr-1 catalyst, Si-substituted norbornenes are arranged in the row by activity shown in Fig. 10.[177]

It is seen that the highest activity in ROMP is exhibited by *exo*-5-trimethylsilylnorbornene (*exo*-SiNB) and 3-trimethylsilyltricyclononene (SiTCN). The effect of substituents in tricyclononenes is less pronounced than in norbornenes and norbornadienes due to the *exo*-arrangement of the cyclobutane moiety and a larger distance between the substituent and the double bond. As a result, *syn*- and *anti*-isomers SiTCN polymerize at similar rates, which differs from the behaviour of the *exo*- and *endo*-substituted norbornenes. Tricyclononenes with two Me_3Si substituents are more active than norbornenes with the same number and arrangement of substituents. Norbornadienes are less active in ROMP than norbornenes. For *gem*-Si2NB, for example, ROMP does not occur under the action of Gr-1. Quantum-chemical calculations of energies and electronic and structural characteristics of monomers of this series give the row of activity analogous to that in Fig. 10.[177]

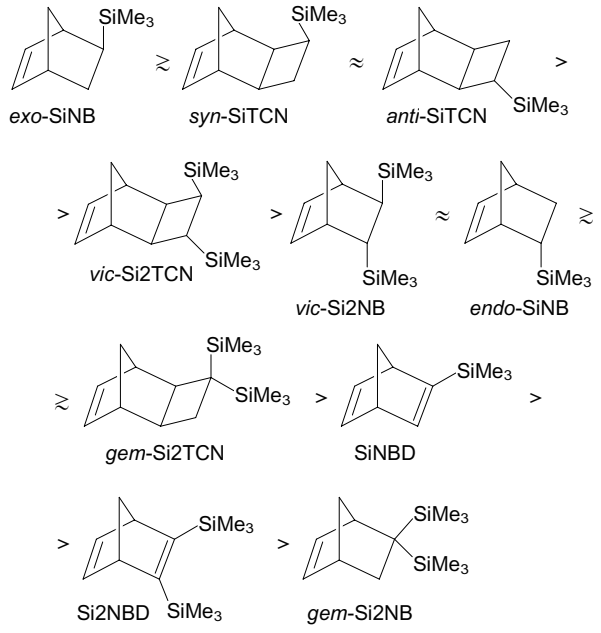
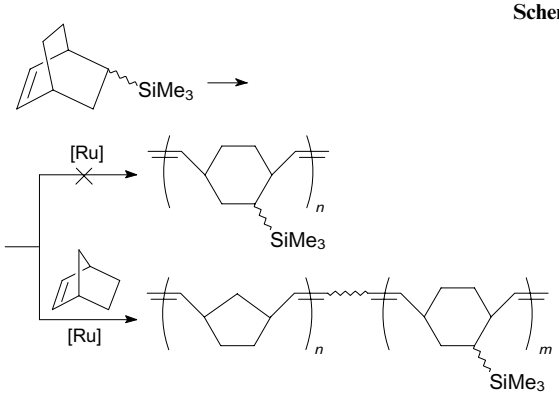


Figure 10. The row of activity of silicon-substituted norbornenes in ROMP catalyzed by Grubbs catalyst of the first generation (the scheme is made by the authors of this review on the basis of reported data [177]).

Norbornene as an active monomer is used in copolymerization for introducing inactive molecules into the polymer chain. For example, low-strained 5-trimethylsilylbicyclo[2.2.2]oct-2-ene does not polymerize in the presence of Grubbs catalysts of the first and second generation as well as a Grubbs – Hoveyda catalyst of the second generation; however, it is involved in copolymerization with norbornene (Scheme 30).[178]

Scheme 30



The ability of metal carbene complexes to accomplish living polymerization of cycloalkenes made ROMP a potent tool for producing macromolecules with controlled length and structure of the backbone and required side substituents (including functionalized substituents) and allowed one to produce block-, graft- and other copolymers of complex architecture.

The advances in macromolecular design of polynorbornenes with important applied properties before 2015 have been largely reflected in monograph [136] and collected works.[137, 138] This is synthesis of biodegradable, biologically active, biorenewable and self-healing polymers, functional and monolith supports, nanoparticles and so on.[136 – 138]

In this review, we dwell on the works that appeared after the publication of the above monographs, mainly in 2015 – 2018.

In macromolecular design of polynorbornenes, the following approaches are mainly used, which are based on the ease of introducing different substituents into the monomer molecule, the possibility of carrying out living polymerization and the presence of reactive double bonds in the polynorbornene backbone or reactive groups in substituents:

— introduction of necessary substituents in the monomer molecule;

— polymerization metathesis of norbornenes to produce homopolymers;

— synthesis of copolymers of different structure *via* copolymerization of monomers, namely, synthesis of ran-

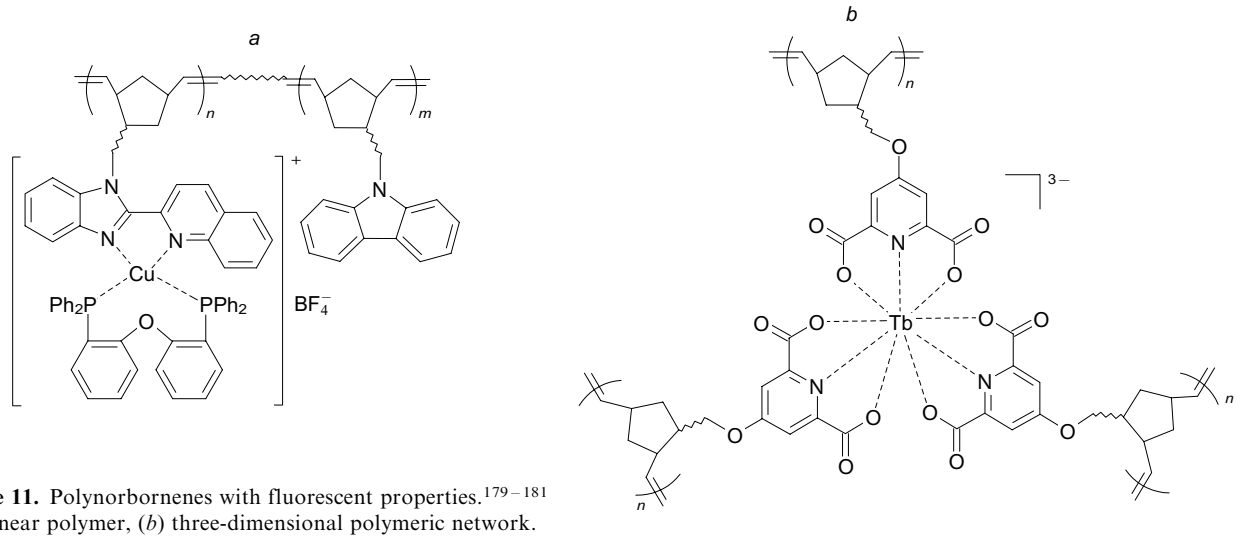


Figure 11. Polynorbornenes with fluorescent properties.[179 – 181] (*a*) Linear polymer, (*b*) three-dimensional polymeric network.

dom copolymers, block-copolymers, alternating or gradient copolymers, polymers of complex architecture with the use of so-called telechelics (macromolecules with functional groups at the ends), macromonomers, as well as a combination of ROMP with various other reactions;

— post-functionalization of polynorbornenes with the use of reactive side groups and double bonds in the backbone.

For norbornenes, ROMP is an efficient approach to the fabrication of materials with fluorescent properties. As a rule, these are norbornene copolymers with bulky carbazole- and(or) metal-containing substituents. Metal-containing complexes are introduced as substituents into the norbornene molecule and then the resulting species is copolymerized with a norbornene molecule containing a less bulky substituent (Fig. 11 *a*).[179, 180] Three-dimensional polymeric networks have also been produced through the ROMP of lanthanide (Eu^{III} and Tb^{III}) monomeric complexes containing three norbornenyl groups (see Fig. 11 *b*).[181] These structures have been synthesized in the presence of highly active Gr-2 and Gr-3 catalysts, since a bulky substituent reduces the polymerization activity of norbornene.

A noticeable number of publications have focused on the search for efficient materials for polymeric anion- or proton-exchange membranes for fuel cells. These are copolymers of DCPD with norbornenes with ester, sulfonyl chloride[182] and ethoxy-containing substituents.[183] The DCPD units are used for cross-linking.

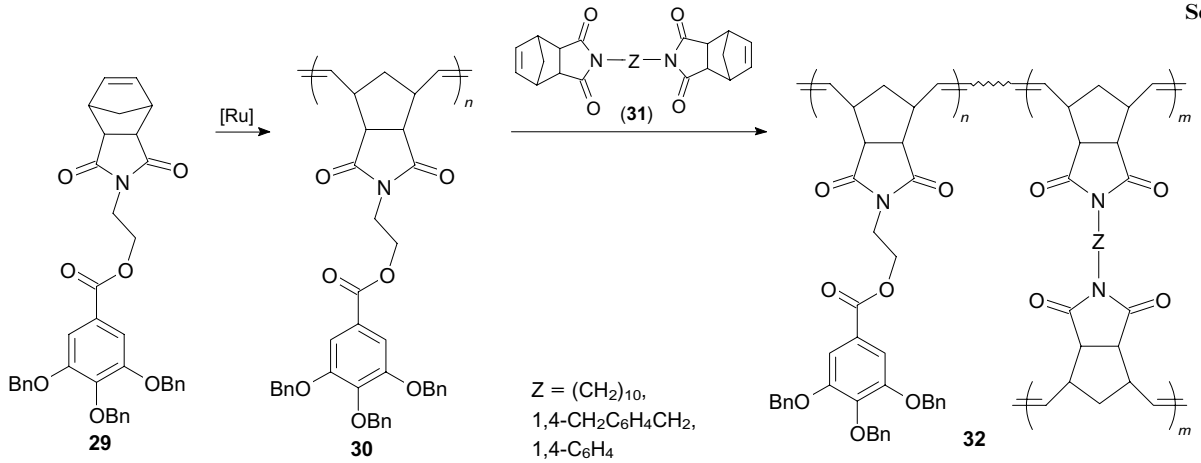
To create materials with enhances gas permeability, silicon- or fluorine-containing substituents are introduced into the starting norbornene molecule, and then it is polymerized, is particular, by the ROMP scheme.[7, 12]

Of interest is the use of ROMP for creation of self-healing materials used, for example, in aerospace engineering.[184] The healing agent as microcapsules is placed into a polymeric matrix (epoxy resin or related composite material) in which the OM catalyst is suspended. When the material is cracked, capsules are destroyed, and the healing agent contacts the catalyst and polymerizes under its action, cross-linking with the polymeric matrix. As the healing agent, DCPD or its mixture with ethylidenenorbornene and norbornene is used. Recently, it has been suggested to use renewable biofeedstock — isosorbide, which is built into the silicon-substituted norbornene,[185] or norbornenes with polymeric ionic liquids and various counterions. The size of counterions has an effect on the strength of the physical cross-link of a polymeric ionic liquid. Larger counterions form weaker and less compact ionic aggregates with imidazolium.[186]

Norbornens are successfully used to synthesize highly branched structures, among which are grafted copolymers: polymeric brushes, star-shaped polymers and dendrimers. Star-shaped polymers are an assembly of chains connected to the common centre. They combine chemical functionality of their chains with the compact shape, high density of the terminal groups and the core – shell structure similar to that of micelles. This determines their application as additives to improve viscosity characteristics of oils,[187] for biomedical purposes — drug delivery[188] *etc*. Among recent works, noteworthy is the synthesis of star-shaped polynorbornenes from a benzyl-wedge monomer (a monomer with three benzyloxy substituents), *i.e*. the synthesis of many-arm chains (Scheme 31, monomer **29**).[189] Monomer **29** under controlled ROMP catalyzed by Gr-3 forms monodisperse polymer **30**. To polymer **30**, cross-linking agent **31** containing two norbornenyl moieties is added to give star copolymer **32**. The degree of cross-linking depends on the length of the Z bridge in the cross-linking agent.

For norbornenes, ROMP is a convenient method of synthesis of one of the types of polymeric brushes, namely, bottle-brush polymers (BBPs). This is a graft-polymer in which one or more side polymer chains are grafted to each unit of the linear backbone chain. This leads to the high density of the grafted chains.[190, 191] The unusual architecture of BBPs is responsible for their unique propeties: entanglement that appears at very high molecular weights, rapid self-assembling to form large domain structures (up to several hundreds of nanometres) and the ability to form micelles in a selective solvent. They have a significantly lower critical micelle concentration as compared with linear diblock-copolymers. This makes it possible to use them for visualization and detection in biological media where the dilution is required. Homopolymers (Fig. 12 *a*), block-copolymers (Fig. 12 *c*) and core – shell structures (Fig. 12 *b*) can be obtained.

Scheme 31



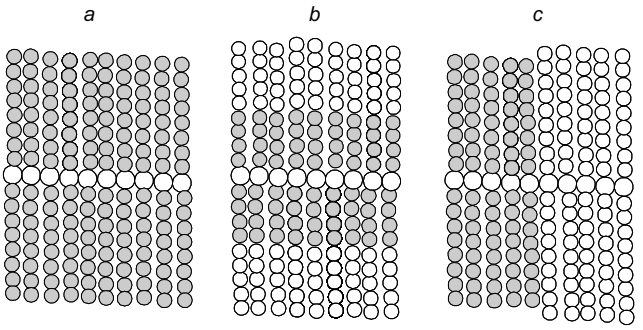


Figure 12. Various types of bottle-brush copolymers (polymer brushes are shown in section).[190, 191]
(*a*) Homopolymer, (*b*) core – shell structure, (*c*) block-copolymer.

Side chains can be functionalized by substituents imparting desired properties to BB copolymers (BBCs). The major areas of use of BBCs are nanocontainers for drug delivery, photonics and lithography.[190, 191]

In photonics, the ROMP of norbornene and its derivatives is used to synthesize photonic crystals. The structure of a photonic crystal is characterized by a periodic change in the refractive index in different directions. BB block-copolymers are self-assembled to form lamellas that are packed in alternating layers, which is responsible for the change in properties in different directions. For BBC synthesis, the ROMP of a norbornenyl macromonomer is, as a rule, used.[192] This provides BBCs with a side chain in each monomer unit. Efficient Gr-2 and Gr-3 catalysts make it possible to synthesize BBCs with a high molecular weight and a narrow molecular weight distribution (MWD), which is especially important for synthesis of photonic crystals. Recently, BBCs with an ultrahigh molecular weight (M_w = 2928 – 3055 kDa) and a narrow MWD (M_w/M_n = 1.07 – 1.13) have been synthesized from norbornene-containing macromonomers.[193] Macromonomers — polystyrene and poly(4-*tert*-butoxystyrene) with the end norbornenyl group (Scheme 32, macromonomers **33** and **34**) — have been synthesized by amidation between a norbornenyl-containing ether with polystyrene with the end amino group. The latter have been synthesized by living anionic polymerization of styrenes.[193] Metathesis polymerization of macromonomers in the presence of the Grubbs catalyst of the third generation gave homopolymers **35**, as well as block-copolymers **36** by successive addition of macromonomers. It has been found that BBCs with an ultrahigh molecular weight are self-assembled into periodic lamellar structures with phase separation and demonstration of colours from blue to pink.

Analogously, BBCs for biological and medicinal purposes — drug delivery matrices and sensitive materials for biosensors — have been synthesized. In particular, polynorbornene brushes with polypeptide side chains have been synthesized.[194] Comb-like[195] and ladder polymers[196] have also been synthesized.

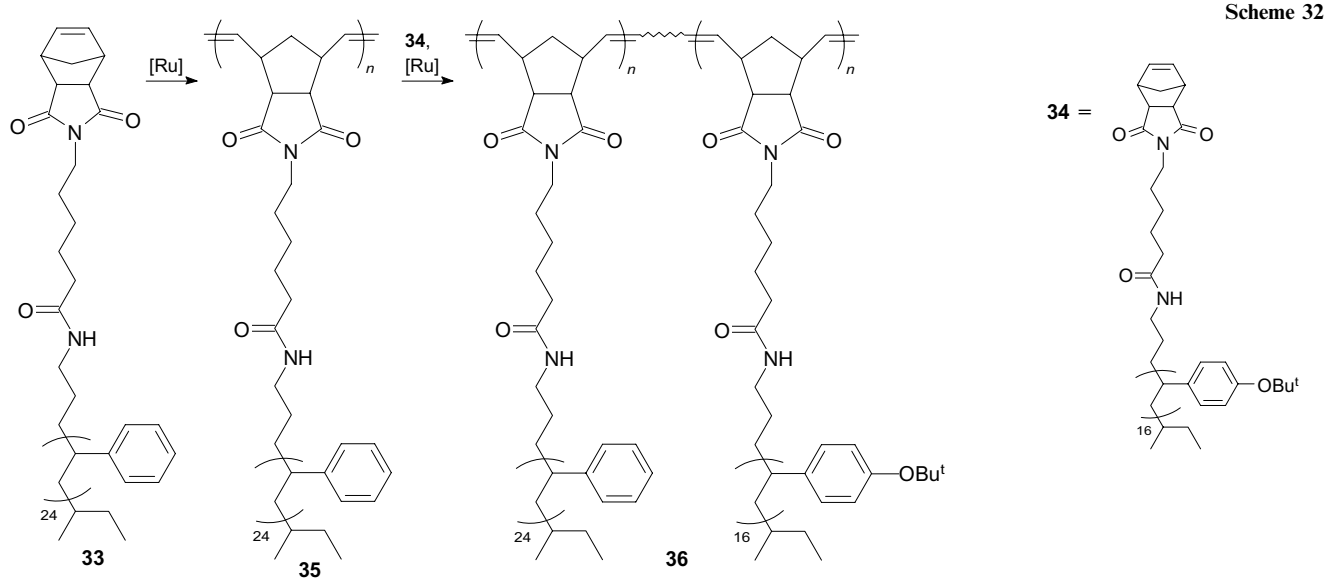
Numerous publications have addressed the creation of hybrid organic-inorganic materials with the use of the ROMP of norbornenes. To obtain nanocomposite materials, covalent binding of organic macromolecules with various inorganic nanosized substrates is used. Attractive objects for such studies are polyhedral oligomeric silsesquioxanes (POSS). The POSS structures have been introduced into norbornene as substituents with subsequent copolymerization with unsubstituted norbornene (Scheme 33).[197]

Synthesis of nanocomposite materials has also been accomplished by surface-initiated ROMP (SI-ROMP) with grafting polymer chains to different surfaces.[137] The surface is first treated, for example, with 5-trichlorosilylnorbornene or linear alkenylsilanes, which interact with the surface hydroxy groups (Scheme 34).[198] Then, the Grubbs Ru carbene complex is added to the norbornene moiety, to give the initiator that performs the ROMP of norbornene or its derivatives on the surface.[199]

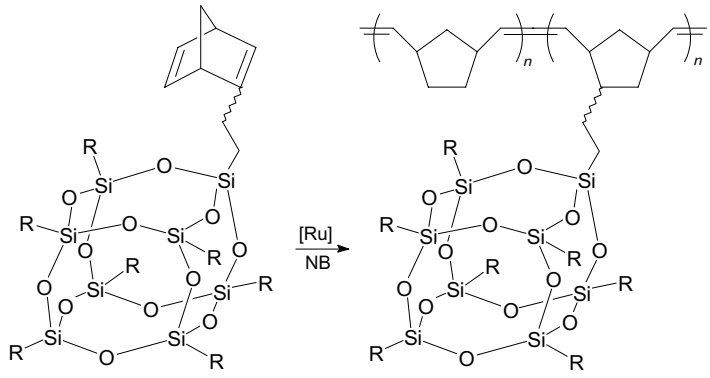
Grafting polymer chains to 5-(perfluorooctyl)norbornene on microstructured coatings has been used for producing superhydrophobic surfaces.[200]

The presence of double bonds in the backbone chain of polynorbornenes synthesized by the ROMP method is responsible for their chemical and oxidative instability on storage.[201] Recently, a polynorbornene has been synthesized, being a copolymer with a small content of monomer units with a sterically shielded phenol (for example, 2,5-diisopropylphenol) moiety in the substituent — the inhibitor of radical reactions.[202, 203] The most general and simplest method of stabilization of polynorbornenes is the hydrogenation of double bonds.[136] Stability and improvement of mechanical and other properties are achieved by cross-linking of polynorbornenes. In particular, polymers of

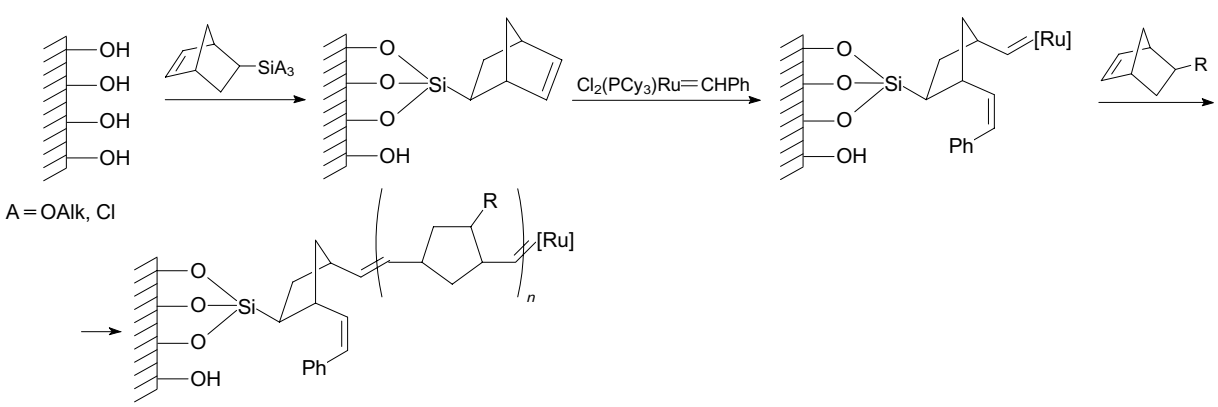
Scheme 32



Scheme 33



Scheme 34

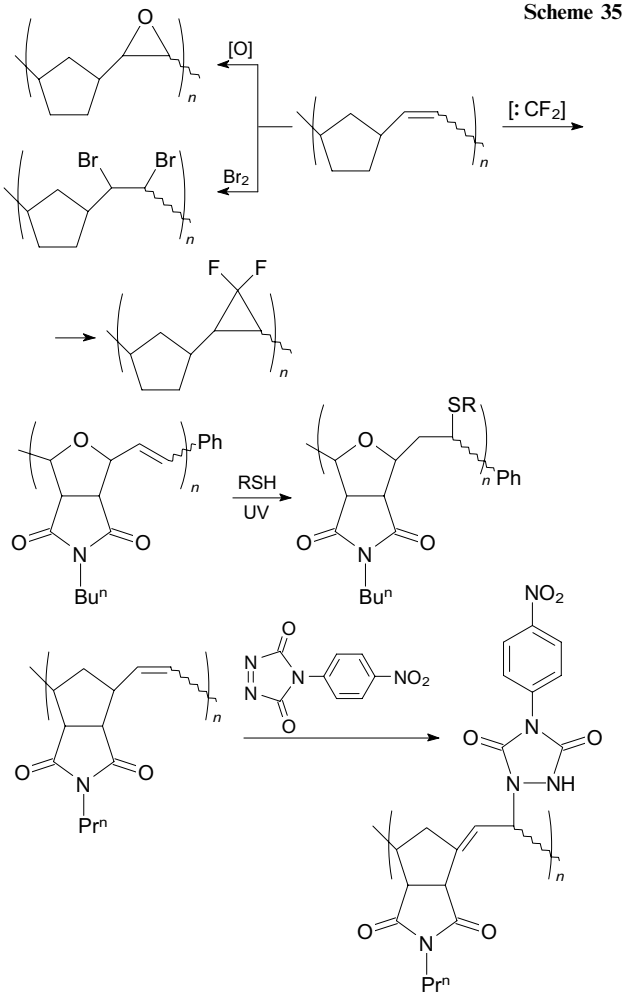


dimethyl 5-norbornene-2,3-dicarboxylate cross-linked by means of ROM copolymerization with bi- and trifunctional norbornene comonomers exhibit good mechanical properties.[204] Cross-linked polymers are also obtained using thiols.[205] A considerable improvement of properties of the polydimethylsiloxane (PDMS) gas separation membrane has been achieved by the ROMP cross-linking of norbornenyl end groups in PDMS.[206]

Functionalization of double bonds of the backbone chain is also an efficient method of tailoring polynorbornene properties. Bromination,[207, 208] epoxidation,[209 – 211] sulfonation,[212] the use of thiol – ene reactions ('click' reaction of thiols with double bonds)[213] and Diels – Alder reactions[214] for modification of polynorbornenes have been described (Scheme 35). Thiol – ene transformations were used to synthesize photoresists[205] and epoxidation and *gem*-difluorocyclopropanation was employed to improve the gas separation properties of polynorbornenes.[215, 216]

Post-polymerization modification of side groups in polynorbornenes is widely used for functionalization. The thiolactone ring in the side substituent is opened under the

Scheme 35

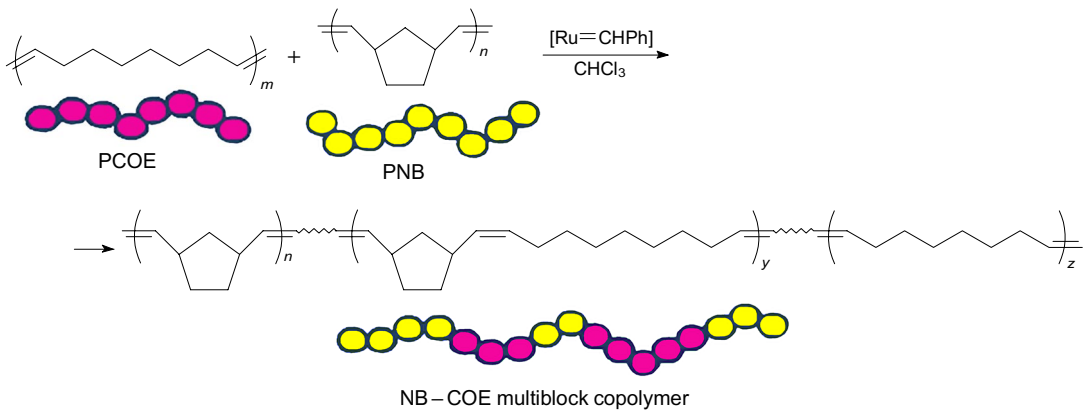


action of amine and reacts with benzyl acrylate by the click reaction to increase the molecular weight of polynorbornene.[217] Imidazole and morpholine fragments are introduced into the side chain of polynorbornene by aminolysis of methyl carboxylate substituents.[218]

The high activity of unsubstituted norbornene in ROMP creates some difficulties for synthesis of its copolymers. For example, the copolymerization of norbornene and cyclooctene is hindered due to the difference in polymerization activity because of the differences between the strain energies of molecules. The strain energy of norbornene is 100 kJ mol^{-1}, $-\Delta G^{\circ}_{ROMP}$ = 47 kJ mol^{-1}, while the strain energy of cyclooctene (COE) is 16 kJ mol^{-1} and $-\Delta G^{\circ}_{ROMP}$ = 13 kJ mol^{-1} (Ref. 136). The copolymerization of norbornene with considerable excess of COE was carried out in the presence of classical catalysts and the Gr-1 catalyst.[219, 220] Nevertheless, it has been detected that the norbornene polymerization occurs first and then the COE polymerization begins. As a result, a mixture of copolymers enriched in one of the components is formed. An analogous situation is observed for the copolymerization of norbornene and tetracyclododecene (which is, in essence, a norbornene derivative because it contains the norbornene moiety in its molecule) with COE on (arylimido)vanadium(V) alkylidene complexes.[221] NB – COE copolymers with a high alternation degree have been synthesized on specially synthesized catalysts.[222 – 224] Another approach to the synthesis of NB – COE copolymers is the replacement of norbornene by its derivatives with substituents decreasing its reactivity.[225] Sometimes both approaches are used by introducing a norbornene derivative into alternating copolymerization with COE on catalysts providing stereoselectivity.[226] It is of interest that a Gr-3-based catalyst into which a quinone fragment was introduced changes its activity as a result of redox reactions under the action of $CoCp_2$ and $FcPF_6$; in one form, it catalyzes the polymerization of the substituted norbornene and in the other form, it catalyzes the polymerization of COE.[227]

Recently, a new approach to the synthesis of NB – COE copolymers has been suggested through the cross-metathesis of their homopolymers (Scheme 36).[228] The reaction products are multiblock-copolymers; the block length and thermal and crystalline properties of these copolymers can be regulated by simple selection of reaction conditions.[229, 230] This method removes the limitations for synthesis of norbornene – COE copolymers caused by the different activity of the monomers, since it proceeds from polymers. In the course of cross-metathesis, the polymeric chain fragments are exchanged at double bonds. Such an approach makes it possible to obtain copolymers of unsubstituted norbornene with substituted cyclooctenes, for example, with 5-hydroxycycloocten-1-ene, which is a more challenging task.[231]

Scheme 36



4.2. Addition polymerization of norbornenes

Vinyl (addition) polymerization (AP) of norbornene and its derivatives (see Scheme 28, reaction *2*) and their copolymerization with ethylene and other alkenes is of interest because of the unique properties of reaction products — addition polynorbornenes and copolymers of norbornene with alkenes classified with so-called cycloolefin (co)polymers (COP and COC).[118, 119, 232 – 234] Their properties and application is discussed in more detail in Section 5. As distinct from addition polynorbornene (APNB), which has a very high glass transition temperature (T_g), copolymers of norbornene with ethylene, propylene and other alkenes can have different T_g depending on the ratio of comonomer units and, therefore they are more suitable for processing. In addition, copolymers are more soluble in hydrocarbons than the homopolymer. Their microstructure has been studied rather well by NMR spectroscopy. Catalysts capable of performing living and quasiliving copolymerization and providing copolymers with a narrow MWD and different comonomer unit ratio have been found.[232, 235, 236]

The introduction of side substituents, especially bulky and functional groups, into the rigid norbornene molecule often leads to an abrupt decrease or complete loss of activity in addition polymerization.[118, 119, 237 – 240]

In recent time, attention has mainly focused on the development of efficient catalytic systems for AP of norbornenes.[118, 119, 232 – 234] On the basis of their composition, AP catalysts can be conventionally divided into two groups: (1) systems based on early transition metal compounds — Ti, V and Zr, especially zirconocenes currently mainly used for copolymerization of norbornene with ethylene; (2) systems based on late transition metal compounds. These are rather rarely used Cr, Fe, Co and Cu complexes as well as the Ni^{II} and Pd^{II} catalysts most active in AP of norbornene.

As a rule, for the AP of norbornenes, these complexes require activation by a cocatalyst. For activation, methylalumoxane (MAO) is used most often; $AlEt_3$, tris(pentafluorophenyl)borane $B(C_6F_5)_3$, trityltetrakis(pentafluorophenyl)borate $[Ph_3C]^+[B(C_6F_5)]_4^-$ and boron trifluoride etherate $BF_3 \cdot Et_2O$ are applied more rarely. In addition, a combination of $B(C_6F_5)_3$ and $AlMe_3$ leads to the easy exchange of aryl and alkyl groups to give BMe_3 and $Al(C_6F_5)_3$. With an increase in the length of the alkyl moiety, the exchange rate considerably decreases. A key role of cocatalysts is in formation of the metal – carbon bond necessary for polymerization initiation.

The cationic $[Pd(NCR)_4]^{2+}X_2^-$ complexes containing weakly bonded nitrile ligands and a weakly coordinated counterion, such as BF_4^-, are active without cocatalyst.

Among the AP catalysts of NB synthesized in recent years, the most active are Ni and Pd complexes presented in Table 4. The Table summarizes complexes exhibiting activity of 10^7 g APNB per mole of a metal in 1 h and higher. As is seen, all catalysts require activation, for which MAO is mainly used.

Of considerable interest are the AP mechanism and the APNB microstructure; however, they are little understood because of the low informativity of its NMR spectra. Periodically, contradictive information on the existence of APNB with 2,3- and 2,7-connections of monomer units has appeared.[260, 261] Even less understood is the polymerization mechanism and microstructure of substituted norbornenes. By now, it has been demonstrated that, at early stages, AP in the presence of many catalysts involves the coordination and *cis-exo*-insertion of the norbornene molecule into the M – C or M – H (M is metal atom) bond of the catalyst.[262] In particular, the addition of the first norbornene molecule to the cationic catalyst $[(All)Ni(MesH)]^+[BAr_4^F]^-$ [Ar^F = 3,5-$(F_3C)_2C_6H_3$] gives the mesitylene σ,π-complex shown in Fig. 13 *a*.[262, 263] In the reaction with an analogous Pd complex, norbornene acts as a bidentate ligand and forms a γ-agostic intermediate (Fig. 13 *b*).[262] The nature of the active centre performing the chain propagation in the AP of norbornene on the cationic complex $[(tmeda)Pd(OEt_2)(Me)][B(Ar^F)_4]$ (tmeda is tetramethylethylenediamine) has been proved by NMR and X-ray diffraction.[263] It has been demonstrated that the unsaturated metal centre is stabilized by the agostic interaction with the hydrogen *endo*-γ-atom of the previous monomer unit of the growing polymer chain (Fig. 14, violet fragment). The found structure of the active centre considerably differs from the structure observed in polymerization of alkenes, which is stabilized by the β-H-agostic interaction.

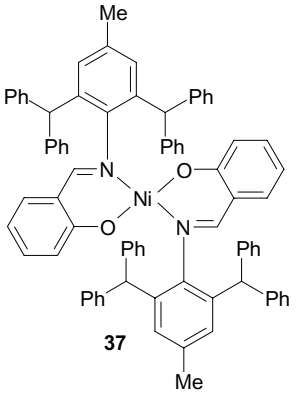
The end groups in low-molecular-weight poly(2-acetoxymethylnorbornene) obtained on the $[Pd(MeCN)_4][BF_4]_2$ and $[(\eta^3\text{-All})Ni(\eta^2\text{-OC(O)}CF_3)]_2$ catalysts have been studied.[264] It turned out that, in addition to the norbornenyl end group (Fig. 15 *a*), there are both endo- and exocyclic end double bonds.

To explain this fact, it has been assumed that a structure is formed (see Fig. 15 *b*) containing both the endo- and exocyclic double bond. Formation of such end units is possible if the bicyclic structure is rearranged to the mono-

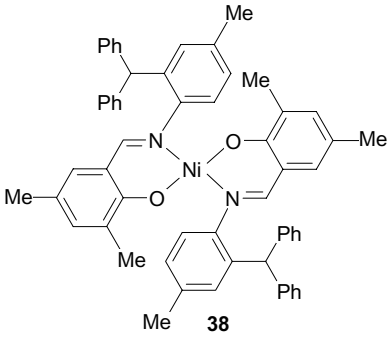
Table 4. Most active Ni- and Pd catalyst of addition polymerization of norbornene.

Catalyst	Activity /g APNB (mol M)$^{-1}$ h^{-1}	Ref.	Catalyst	Activity /g APNB (mol M)$^{-1}$ h^{-1}	Ref.
37 + MAO	to 1.3×10^7	241	**46** + MAO	to 10^8	251
38 + MAO	to 1.913×10^7	242	or $[Ph_3C]^+[B(C_6F_5)_4]^-$		
39 + MAO	1.98×10^7	243	**47a**,**b** + MAO	10^7	252
Ni(COD) + $BF_3 \cdot Et_2O$	1.93×10^6	244	**48** + $BF_3 \cdot Et_2O$	$10^5 – 10^7$	253
40 + MAO	1.94×10^7	245	**49a**,**b** + MAO	10^7	254
41 + MAO	to 5.82×10^7	246	**50** + MAO, MMAO	to 4.8×10^8	255
42 + MMAO	to 5.46×10^7	247	or (activator + AlR_3)		
43 + MAO	to 8.2×10^6 for Ni;	248	**51a**,**b** + MAO	to 10^7	256
	to 2.66×10^8 for Pd		**52** + MAO	9.97×10^6	257
44 + MAO	to 1.668×10^7	249	**53a**,**b** + MAO	10^7	258
45a,**b** + MAO or Et_2AlCl	to 5.99×10^7	250	**54a** – **c** + MAO	10^7	259

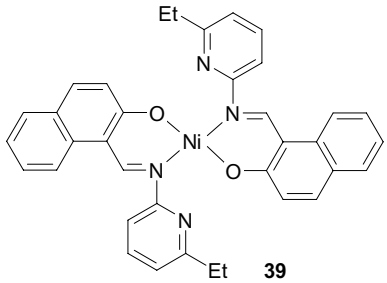
Structures 37 – 51



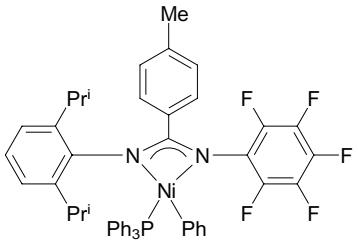
37



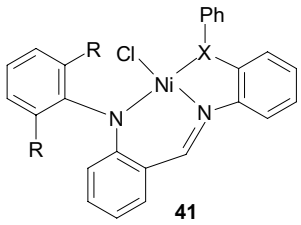
38



39

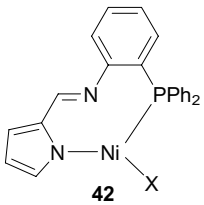


40



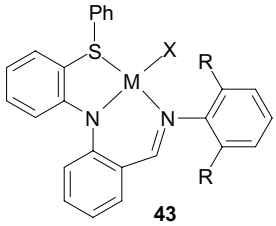
41

X = S, PPh; R = H, Me, Et, Pr^i



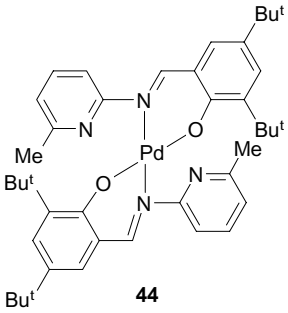
42

X = Cl, Br, I

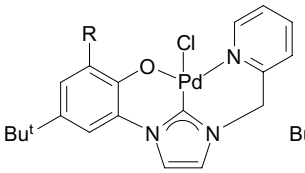


43

M = Ni, X = Br;
M = Pd, X = Me;
R = H, Me, Pr^i

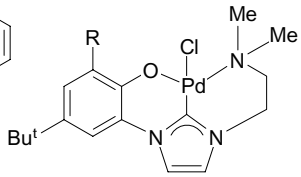


44



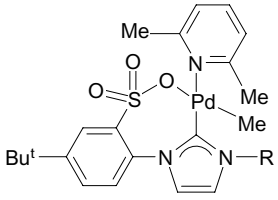
45a

R = H, Bu^t



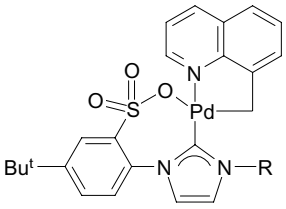
45b

R = H, Bu^t



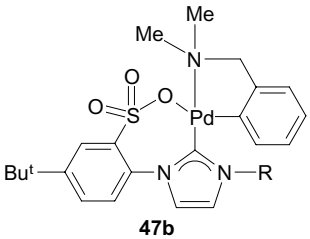
46

R = CH_2Mes, CH_2Ph, Bu^n, Pr^i



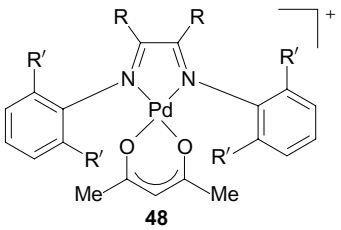
47a

R = Me, Pr^i, Bu^n,
CH_2Ph, CH_2Mes

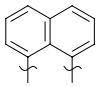


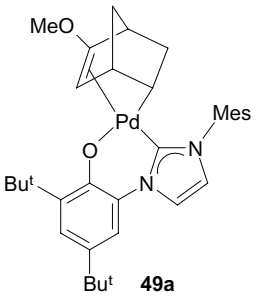
47b

R = Me, Pr^i, Bu^n,
CH_2Ph, CH_2Mes

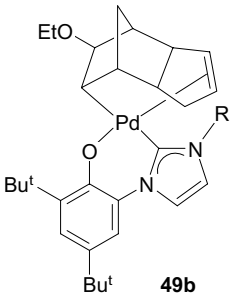


48

R = H, Me; R – R = ;
R′ = Me, Pr^i

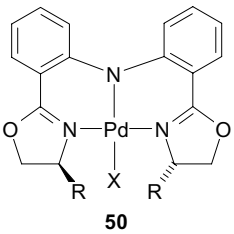


49a



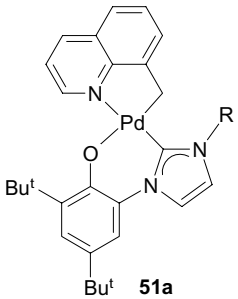
49b

R = Mes, Me, Pr^i, Ph

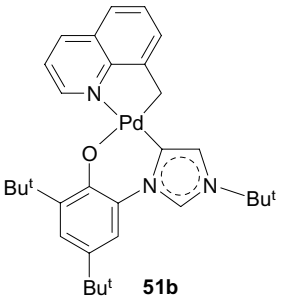


50

X = Cl, OAc, OTf;
R = Pr^i, Ph



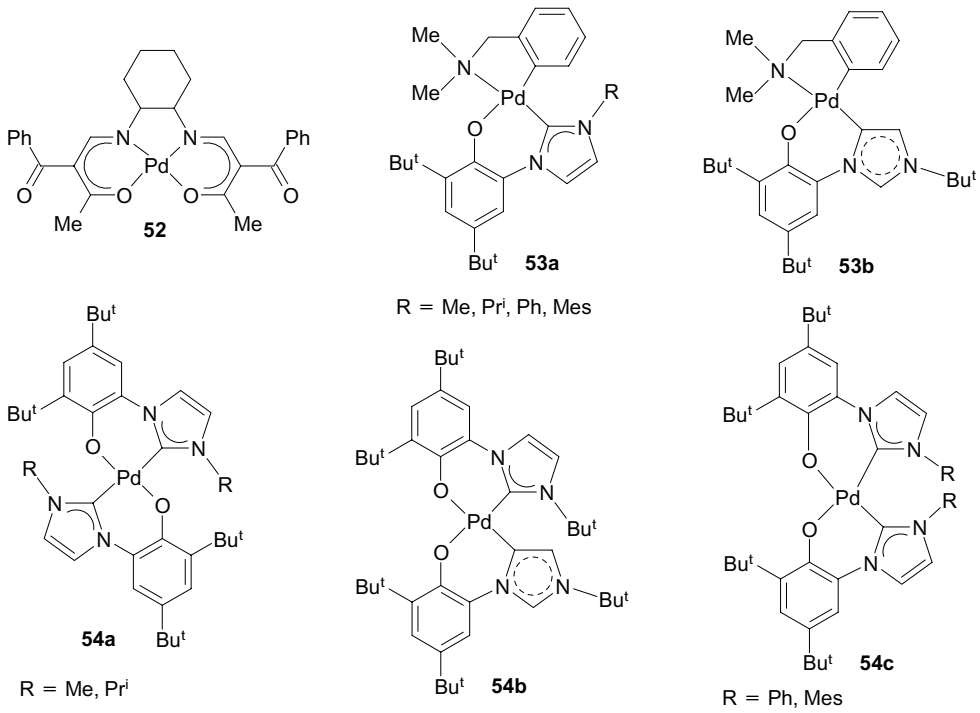
51a



51b

R = Me, Pr^i, Ph, Mes

Structures 52 – 54



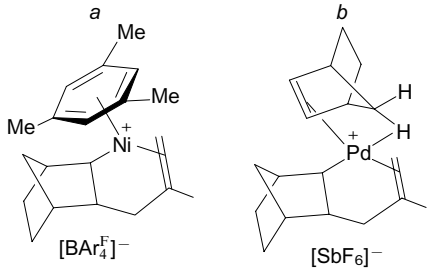


Figure 13. Mesitylene σ,π-complex (*a*) and γ-agostic intermediate (*b*) forming in the reaction of norbornene with cationic Ni and Pd catalysts.[263]

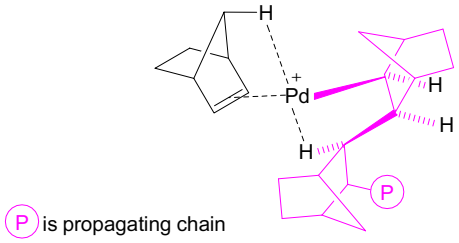


Figure 14. Structure of the active centre performing the chain growth in addition polymerization of norbornene on the cationic complex [(tmeda)Pd(OEt$_2$)(Me)][BAr$^F_4$].[263]

cyclic one through the cleavage of the bond between the β- and γ- carbon atoms of the methylene bridge. The Pd atom migrates to the former methylene carbon atom of the bridge. In the resulting intermediate, the Pd atom can readily occupy the position required for the H-elimination from the tertiary carbon β-atom, which leads to the formation of the exocyclic double bond. The Pd – H hydride complex is able to further initiate the formation of a new polymer chain.[264]

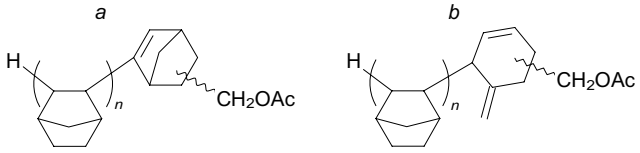


Figure 15. Structure of end groups in poly(2-aacetoxymethyl-5-norbornene) obtained on the [Pd(MeCN)$_4$][BF$_4$]$_2$ and [(η^3-All)-Ni(η^2-OC(O)CF$_3$)]$_2$ catalysts.[264]
(*a*) Norbornenyl end group, (*b*) structure with endo- and exocyclic double bonds.

The microstructure of APNB has been studied. The presence of two stereo centres in a monomeric unit (tertiary carbon atoms in a polymer chain) as well as three different types of unit connections (*endo* – *endo*, *exo* – *exo*, *endo* – *exo*) determine the microstructure of APNB. Therefore, six stereoregular APNB structures can hypothetically exist under the condition of the *cis*-opening of the double bond (Fig. 16).[118]

Studies of polynorbornene synthesized on zirconocene catalysts are complicated because it is insoluble in organochlorine and other solvents even at elevated temperatures. At the same time, in the presence of the *rac*-[{CMe$_2$(Ind)$_2$}ZrCl$_2$] – MAO (Ind is inden-1-yl) catalyst, crystalline di-, tri-, tetra- and pentamers of norbornene have been synthesized (in the presence of hydrogen), and two types of binding in their chain (2-*exo*, 7′-*syn*) and meso-structural elements have been detected [265] (Fig. 17).

It has been recently shown that the Pd complex with an imine-N-heterocyclic carbene ligand activated by MMAO catalyzes, in the presence of hydrogen, the oligomerization of norbornene to give bonds to the C(7) atom.[266] The

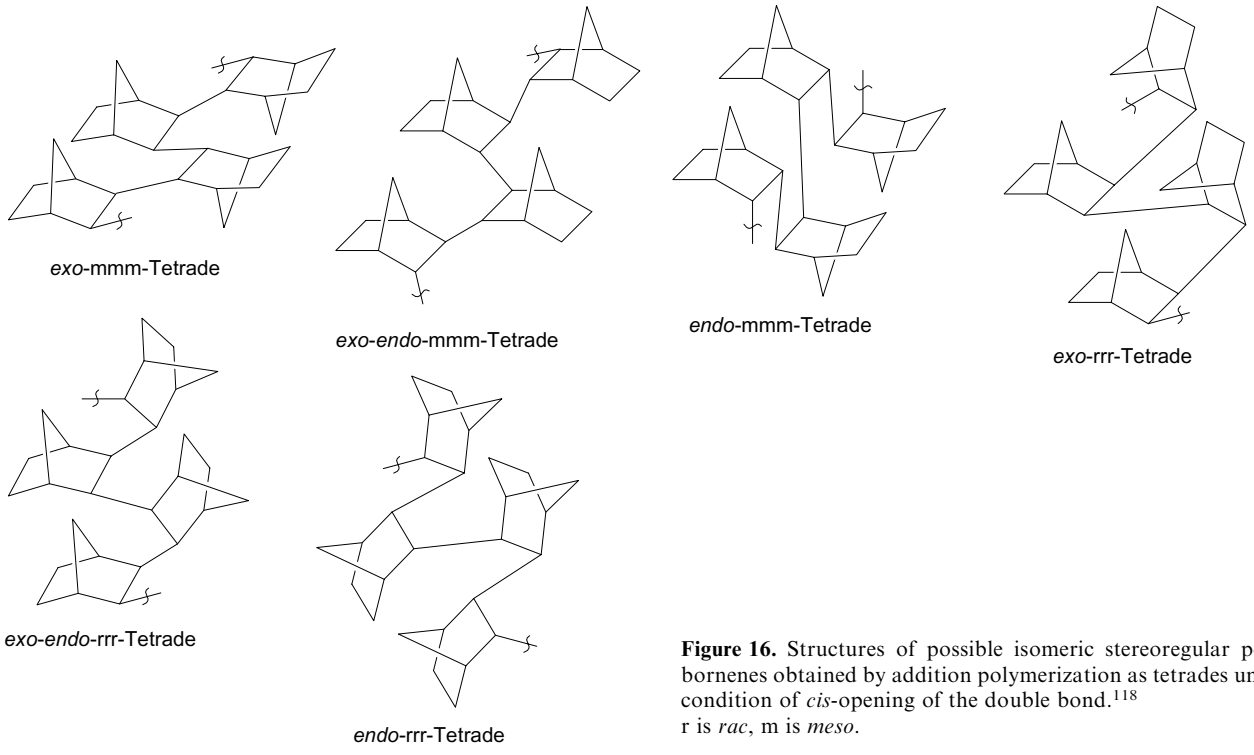


Figure 16. Structures of possible isomeric stereoregular polynorbornenes obtained by addition polymerization as tetrades under the condition of *cis*-opening of the double bond.[118]
r is *rac*, m is *meso*.

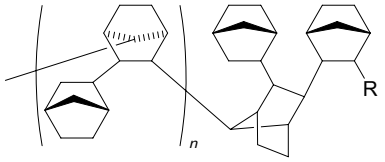


Figure 17. Two types of binding in the APNB chain: 2-*exo* and 7′-*syn*.[265]

authors believe that this is a probable reason for the insolubility of APNB synthesized on Pd systems. Generally, the formation of insoluble polynorbornenes is rather frequently encountered for the addition polymerization of NB. Polynorbornenes readily soluble in chlorine-containing solvents and cyclohexane are formed mainly on Ni catalysts. For example, in the presence of the Ni complex with the anilinonaphthoquinone ligand activated by $B(C_6F_5)_3$, soluble APNB with $M_n = 520\,000 - 660\,000$ Da and $M_w/M_n = 2.13 - 2.97$ has been synthesized.[267]

From the APNB synthesized on the $CrCl_2$(dppa) – MAO catalyst [dppa is bis(diphenylphosphino)amine], the crystalline part has been isolated, which contains a regular sequence of mr-triads — 2,3-*exo*-diheterotactic polymer with two types of end units of macro chains (Fig. 18).[268]

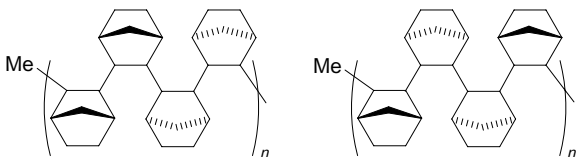


Figure 18. 2,3-*exo*-Diheterotactic polynorbornene obtained by addition polymerization with two types of end units.[268]

Thus, the APNB microstructure is largely determined by the structure of the active centre and depends on the type of catalytic system.

The APNB synthesized on cationic Ni and Pd complexes is characterized by a rather narrow MWD (1.2 – 1.4 on the Pd complex and 1.4 – 1.9 on the Ni catalyst), which can be evidence of controlled polymerization.[262] However, NMR has demonstrated that, in the course of norbornene polymerization on these catalysts, the initiation is very slow and the chain growth is rather fast, which points to the absence of controlled (or pseudoliving) polymerization. The controlled AP of norbornene and its derivatives has been accomplished on the $[Pd(MeCN)][BF_4]_2$ catalysts[269] and Ti fluorenyl complexes activated by MAO free of trialkylaluminium.[270, 271]

As mentioned above, substituted norbornenes exhibit much lower activity in AP. Detailed analysis of the effect of the type, size and position of the substituent on the course of AP[237] carried out on a Pd catalyst {synthesized *in situ* in the $(COD)Pd(Me)Cl + PPh_3 + [PhNHMe_2][B(C_6F_5)_4]$ system} demonstrates that the major role in the decrease in the monomer activity is played by the ability of the substituent to coordinate to the metal atom of the active centre. The activity of norbornenes in polymerization also decreases with an increase in the substituent size. *endo*-Substituted norbornenes are considerably less active than the corresponding *exo*-isomers, especially when the substituents are able to coordinate or chelate the metal.[272, 273]

The lower activity of *endo*-DCPD in the addition polymerization on $TiCl_4 - Et_2AlCl$ is explained by possible steric repulsion between the *endo*-cyclopentene moieties of neighbouring units, which slows down the successive insertion of two *endo*-isomers.[273] For the *exo*- and *endo*-isomers of

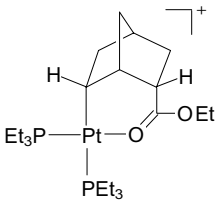


Figure 19. Product of *endo*-insertion of *endo*-ethyl norbornenecarboxylate synthesized on the catalytic system *trans*-$[(Et_3P)_2Pt(H)Cl]-Na^+[3,5\text{-}(F_3C)_2C_6H_3]_4B^-$ (Ref. 274).

partially hydrogenated DCPD, an analogous difference in activity is observed.

It seems that the lower activity of norbornenes with polar substituents in the *endo*-position is explained by the better capacity of *endo*-isomers for coordination to the catalyst as compared with the *exo*-species. For the model catalytic system *trans*-$[(Et_3P)_2Pt(H)Cl]-NaBAr^F_4$, the possibility of *endo*-insertion of *endo*-substituted norbornene into the metal – carbon bond has been demonstrated.[274] The corresponding product of *endo*-insertion of *endo*-ethyl norbornenecarboxylate (Fig. 19) has been isolated, and its structure has been proved by NMR and X-ray diffraction.

The possibility of *endo*-insertion, as distinct from the *exo*-insertion proved for unsubstituted norbornene, can be explained by the initial coordination of the carbonyl group with a metal. Hence, the insertion of subsituted norbornene on the *endo*-side of the double bond will be more suitable.

The influence of a bulky substituent in the *endo*-position becomes evident if the structure of the Pd active centre performing the polymer chain growth is taken into account (Fig. 20).[263] Since the catalytic active centre is stabilized by the agostic interaction of the Pd atom with the *endo*-proton of the previous monomeric unit of the growing chain, the presence of bulky substituent R in the *endo*-position can create steric hindrances for such stabilization.

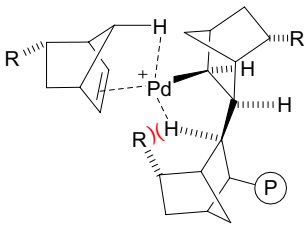
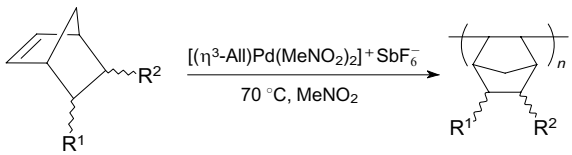


Figure 20. Influence of a bulky substituent in the *endo*-position on the structure of the Pd active centre performing the polymer chain growth in addition polymerization of substituted norbornene. Parentheses)(denote steric repulsion of substituents.

When studying the AP of methyl *exo*- and *endo*-norbornenecarboxylates on the $(Bu^t_3P)Pd(Me)Cl-NaBAr^F_4$ catalyst, it has been shown that the *exo*-isomer polymerizes twice as fast as the *endo*-structure.[272] However, when an equimolar mixture of isomers polymerizes, their AP rates are the same and equal to the polymerization rate of the *exo*-structure.[272] The same activity of isomers in their equimolar mixture was also observed for the AP of methyl norbornenecarboxylate on cationic palladium acetylacetonate complexes with mono- or bidentate phosphine ligands activated by $BF_3 \cdot Et_2O$.[275] It is assumed that the ligand environment in these catalytic systems is able to hinder the chelation of the catalyst by the ester group upon the coordination of the *endo*-isomer.

An interesting way to overcome the inactivity of polar *endo*-substituted norbornenes in AP has been recently suggested.[276] It has been demonstrated that rather efficient AP of norbornenes with polar substituents is possible on the $[(\eta^3\text{-All})Pd(MeNO_2)_2]^+SbF_6^-$ catalyst (Scheme 37). This is due to the tandem activity of the catalyst, which not only performs the AP of norbornenes but also promotes the isomerization of the *endo*-isomer to the *exo*-structure in the course of polymerization. This method allowed the authors to carry out the polymerization of dimethyl norbornene-1,2-dicarboxylate containing 100% of the *endo*-isomer and obtain the polymer in a yield of up to 56% with $M_n = 13\,100$ and $M_w/M_n = 1.3$ (Ref. 276). It is likely that, at elevated temperature (70 °C), the catalyst as a Lewis acid catalyzes the Diels – Alder reaction in the forward and reverse directions. The existence of diene synthesis – retrodiene decomposition equilibrium leads to the transformation of the *endo*-isomer to some amount of the *exo*-isomer, which immediately enters into AP through the insertion into the [Pd] – C bond of the growing polymer chain. As a result, the alternating *exo*-*endo*-polymer is formed. It has also been shown in the same work [276] that the activity of the *endo*-isomer can depend on the type of solvent. A polar solvent inhibits the coordination of the monomer to the catalyst through solvation of the ionic catalyst.

Scheme 37



R^1	R^2	*endo* (%)	Yield (%)
CO_2Me	H	73	65
CO_2Me	CO_2Me	83	75
CO_2H	H	75	57
CH_2OH	H	82	53
CH_2Br	H	86	15
CHO	H	80	73
C(O)OC(O)		0	83
C(O)N(All)C(O)		35	80

Other ways to overcome the low activity of substituted norbornene in AP are their copolymerization with unsubstituted NB and the introduction of required substituents by post-modification of side groups.[277]

Living polymerization of substituted norbornenes has been accomplished on $(Bu^t_3P)PdMeCl-NaBAr^F_4$ (Refs 278, 279) and $(Bu^t_3P)PdMeCl$ activated with $[Li(OEt_2)_{2.5}]B(C_6F_5)_4$.[280] From norbornenes with alkyl, aryl, fluoroaryl and hexafluoroisopropyl substituents, monomodal polymers with a narrow MWD (1.13 – 1.27) have been synthesized. Successive addition of monomers has led to block-copolymers.

It is worth noting that Ti, Co and Ir compounds can initiate both the addition and metathesis polymerization of norbornene depending on the type of cocatalyst and the cocatalyst : catalyst molar ratio.[281] On the iridium catalyst

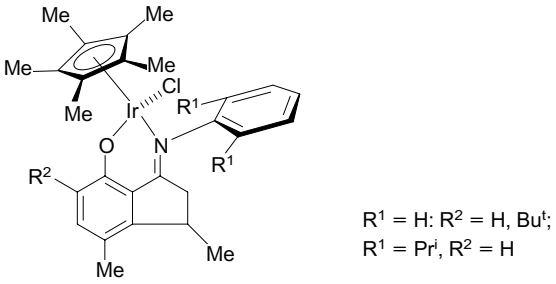
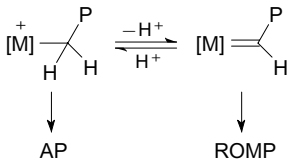


Figure 21. Ir catalyst capable of initiating both the addition and metathesis polymerization of norbornene.[281]

(Fig. 21) at the MAO : catalyst ratio of up to 30 (better 10 – 15), metathesis polynorbornene exclusively forms, while at MAO : catalyst > 50 (better, 2000), only APNB forms.

Based on the hypothesis about the possibility of transition between ROMP and AP through the α-H-elimination — addition reactions (Scheme 38), Buchmeizer[282] has synthesized Zr and Hf complexes, and two of them are shown in Fig. 22. The presence of the 2-pyridyl moiety, in addition to the boron-containing group, and activation with MAO make it possible to synthesize polynorbornene, as well as its copolymer with ethylene, containing different monomer units formed in the ROMP and AP processes. This approach makes it possible to synthesize CO copolymers that are capable of simple post-polymerization fuctionalization at double bonds. The replacement of double bonds by polar groups endows copolymers with adhesion properties required for producing coatings.

Scheme 38



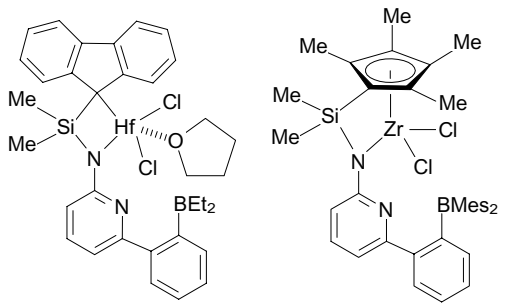


Figure 22. Zr and Hf complexes used for synthesis of polynorbornene and its copolymer with ethylene containing units formed through both ROMP and addition polymerization.[282]

5. Commercially available polynorbornenes

5.1.Metathesis polymerization products

5.1.1.Polynorbornene

Metathesis polynorbornene (MPNB) is the first commercially available ROMP product. Its producion was developed by CdF-Chimie (France) in 1976.[136, 283] Under the trademark Norsorex®, CdF-Chimie produced 5000 tonnes per year of polynorbornene at the Carling plant (Lotharingia, France). Since 1978, this product has also been known as Norsorex® in the United States and Japan. Beginning in February, 2007, polymer Norsorex® has been manufactured by Startech Advanced Material GmbH. Startech works with the well-known brand Astrotech.

Norsorex® is synthesized by polymerization of norbornene in the presence of $RuCl_3 - HCl$ in air, and 1-butanol is used as a solvent.[284] This polymer is a thermoplastic material with a high molecular weight (> 3.0 MDa) and is amorphous. The polymer contains 90% of double bonds in *trans*-configuration.[284] The cyclopentane moiety in the backbone chain of polynorbornene limits the segment flexibility, which is responsible for a relatively high glass transition temperature (35 – 37 °C). Thus, at room temperature, MPNB is solid (glassy). MPNB exhibits stereoisomerism: it can have *cis*- and *trans*-configuration of double bonds in iso- and syndiotactic chains (see Section 4.1, Fig. 5). Depending on the chain stereostructure, physical and chemical properties of the material are different. For example, MPNB with the predominant content of *trans*-C=C bonds in the backbone has the glass transition temperature $T_g \approx 35$ °C, and *cis*-polynorbornene has $T_g \approx 70$ °C.[285]

MPNB can be combined with a large amount of a filler or plasticizing oil. When plasticizers are added, the material exhibits rubber-like properties.[286] The polymer has high affinity for hydrocarbons and can absorb hydrocarbon compounds in amounts 10 times as large as its weight.[287] As Norsorex® APX, it is used as an adsorbent for collecting spilled oil products. It is hydrophobic and thus is insoluble in water. As the adsorbent for hydrocarbons, the Norsorex® APX powder can be used in two steps. In the first step, because of the high adsorption rate, further spread of the oil is prevented in a few minutes (gelation occurs). In the second step, the oil is solidified in a few hours to form an inert continuous rubber-like mass, which can be easily collected and burnt, utilized or used for other purposes (for example, in rubber industry).[287]

Polynorbornene can be blended with common elastomers and cross-linked by sulfur, as well as by means of peroxide curing systems. Vulcanizates of these compositions have a surprisingly high tensile strength and behave as elastomers with high dynamic damping. This property is responsible for their use in noise- and sound-absorbing materials.[288, 289] Polynorbornene was the first shape memory polymer material.[290]

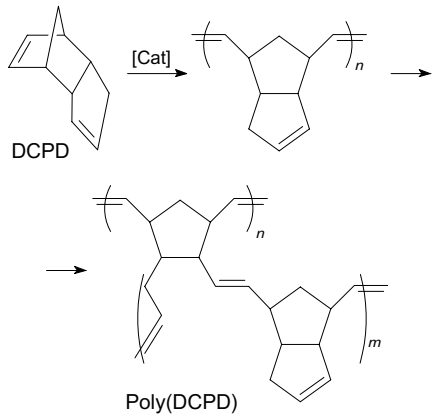
The chemical instability of MPNB is caused by gradual oxidation of the material in air. This can be accompanied by polymer cross-linking. It has been demonstrated that heat in air leads to cross-linking of the MPNB by the oxidative mechanism, which mainly involves *trans*-substituted double bonds. Thermooxidative processes lead to the increase in the specific free surface energy basically due to the increase in the dispersion contribution.[201]

5.1.2. Poly(dicyclopentadiene)

Currently, the best-selling metathesis polymer of the norbornene type is poly(dicyclopentadiene) (approximately 25 000 tonnes per year).[287] It is produced under the trademarks Telene®, Metton®, Pentam® and Proxima. Dicyclopentadiene is an available petrochemical product isolated from the C_5 oil pyrolysis fraction along with CPD. In the course of ROMP of DCPD, the polymer is cross-linked with

participation of cyclopentene double bonds by the metathesis scheme (Scheme 39). Rimtec corporation (manufactures Telene®, Metton® and Pentam®) uses the reaction injection moulding (RIM) tecnology in the presence of homogeneous W or Mo catalysts (WCl_6, $WOCl_4$ or tridodecylammonium octamolybdate).[287] Since the reaction is very fast, two flows containing the monomer are mixed immediately in the mould. One of the flows contains fillers and additives, and the other contains the activator ($EtAlCl_2$ or Et_2AlCl, propanol and $SiCl_4$) and also fillers and additives. The heat released heats the mould to 200 °C, and cross-linking of the product occurs. The reaction is complete in a few minutes. The catalytic system is sensitive to air and impurities in DCPD. Therefore, the latter is thoroughly purified, and the reaction is carried out in an inert atmosphere. The Materia company, producing poly(DCPD) under the trademark Proxima uses the Grubbs Ru catalyst. The technology makes it possible to use a wider range of additives and fillers, because the catalyst is tolerant to functional groups. The high price of Ru catalysts requires their high efficiency. Recently, a large number of latent catalysts, which are active only when heated, have been developed for the polymerization of DCPD (see Section 4.1). This allows one to more accurately control the process of polymerization and get the product of better quality.

Scheme 39



Poly(dicyclopentadiene) has high chemical stability, high impact strength (from 31 to 46 kJ m^{-2}) and low water absorption (weight increase of 0.09% after 24 h in water).[287] These properties are caused by the presence of the bicyclic structure, unsaturated polymer skeleton and cross-linking. The polymer is resistant to corrosion, acids and alkalis mainly because its surface is oxidized. The oxidation is a self-inhibiting process, which leads to the passivation of the surface. The oxidation of the poly(DCPD) surface facilitates its dyeing and glueing.

5.1.3. Hydrogenated metathesis polynorbornenes

Polynorbornene and poly(DCPD) are hydrogenated to enhance their oxidative stability. Hydrogenation of polynorbornene affords a crystalline nontransparent polymer with T_m = 142 – 143 °C.[287, 291] The use of norbornene derivatives, for example, DCPD and others (Fig. 23) results in transparent polymers containing cyclic structures in the backbone and therefore referred to as cycloolefin (co)polymers. Since 1991, Nippon Zeon has been producing polymers under trademarks Zeonex® (10 grades) and Zeonor®

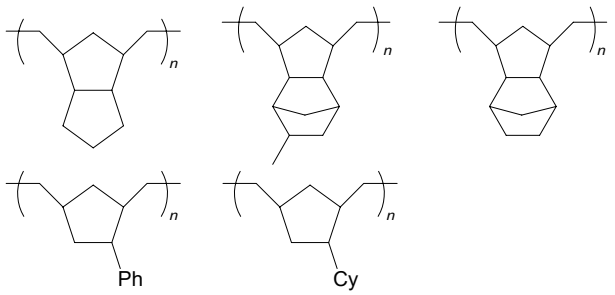


Figure 23. Highly transparent polynorbornenes produced by Nippon Zeon company.[291]

(4 grades); Japan Synthetic Rubber Corporation produces polymers under trademark Arton® (6 grades); all these polymers are produced from norbornenes by the ROMP method with subsequent partial or exhaustive hydrogenation. Zeonex® is an amorphous, colourless transparent polymer with a high glass transition temperature (T_g = 140 °C) and low water absorption.[291] These properties are suitable for using Zeonex® in optical industry (discs, lenses, prisms). Since 1998, the production of amorphous hydrogenated polymer Zeonor® has been implemented. The key difference between Zeonex® and Zeonor® is in that Zeonex® is produced with exact optical characteristics and is used in optical devices, whereas Zeonor® provides improved mechanical properties for parts used in optical, electronic and automobile industry.[291] Zeonex®, Zeonor® and Arton® compete with poly(methyl metharylate) (Plexiglas®) and polycarbonate as well as with addition copolymers of norbornene and ethylene, such as Avatrel®, Apel® or Topas® (see below).

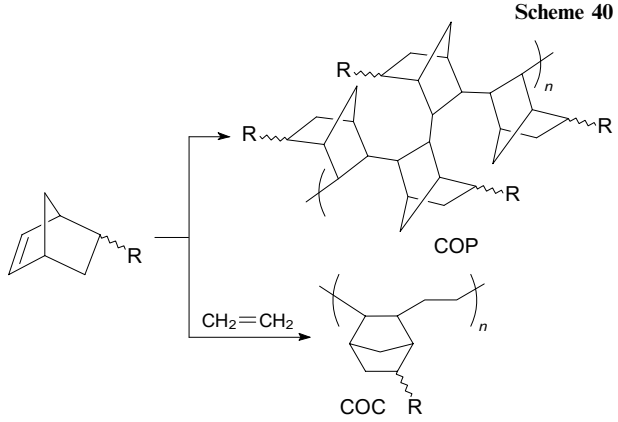
5.2. Product of addition (co)polymerization of norbornene

5.2.1. Homopolymers and binary copolymers

Addition (co)polymers of norbornene are thermoplastic amorphous materials. They have valuable physicochemical properties and are produced from available raw materials of petrochemical origin. Addition polynorbornenes have high transparency, low birefringence, a refraction index of 1.53 coinciding with that of optical quartz and barrier properties to water exceeding those of polyethylene and polypropylene.[234] They are chemically stable to concentrated and dilute mineral acids and alkalis, insoluble in polar solvents, but are soluble in nonpolar solvents, in particular, in cyclohexane. Such polymers have high thermal stability (the decomposition onset temperature is 420 °C).[234] The synthesis of homopolymers of norbornene and its substituted derivatives (COP), as well as the synthesis of norbornene copolymers with ethylene or propylene (COC), are presented in Scheme 40. Promerus LLC company produces homo-, co- and terpolymers based on substituted norbornenes (alkyl-, epoxy-, silicon-substituted) developed by BF Goodrich company under the marks Avatrel, Appear and Duvcor.[292]

Norbornene copolymers with ethylene are the most interesting and universal. The copolymer structure (from random to alternating) and properties can be controlled by selecting proper catalysts. Currently, they are produced under trade marks Topas by Ticona and Apel by Mitsui Chemicals Inc. The latter produces copolymers using vanadium-based catalysts. The copolymers of ethylene and

Scheme 40

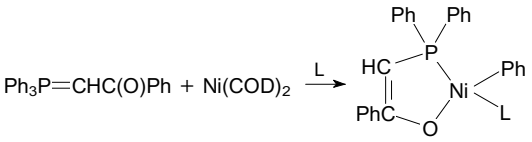


R = H, Alk, epoxy- and Si-containing groups

norbornene are usually amorphous and have a wide range of glass transition temperatures: from room temperature to ~220 °C. They are perfectly processed by traditional methods (injection moulding, extrusion, pneumatic moulding), have a record-low shrinkage ratio (0.6% – 0.7%).[293] Mechanical properties are close to the properties of typical engineering plastics (elastic modulus 2600 – 3200 MPa).[293] These properties make copolymers of norbornene with ethylene competitive materials in various application areas, including the production of pharmaceutical packaging materials and especially for various optoelectronic devices — optical films and lenses, coatings for compact discs (CD) and video disks (DVD), liquid crystal display panels (LCD), *etc*.[293]

Recently, a new efficient Ni system has been developed for the addition copolymerization of norbornene with ethylene (Scheme 41).[294]

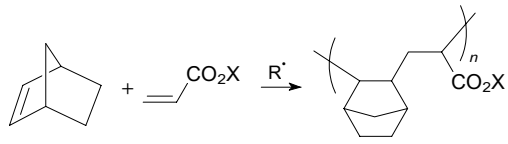
Scheme 41



At L = Py, this complex does not initiate the norbornene polymerization; however, in its presence (molar ratio NB : Ni = 300) and at an ethylene pressure of 3 – 20 atm, copolymerization of norbornene and ethylene occurs in toluene or chlorobenzene. The process is carried out at room temperature in the absence of cocatalysts.[294] This catalyst is available and not expensive, and the resulting copolymers are close in properties to commercial materials like Topas and Apel. It is important that, depending on copolymerization conditions, the copolymers of different composition with glass transition temperatures from 70 to 140 °C can be produced.[294]

New addition copolymers of norbornene with acrylates, namely with *tert*-butyl acrylate (TBA) and methyl acrylate (MA), have been synthesized; this synthesis can be used for producing nanocomposites and materials for optoelectronic devices as DVD coatings, light guides, precision lenses, optical films, flat light guides for LCD, *etc*. The NB

Scheme 42



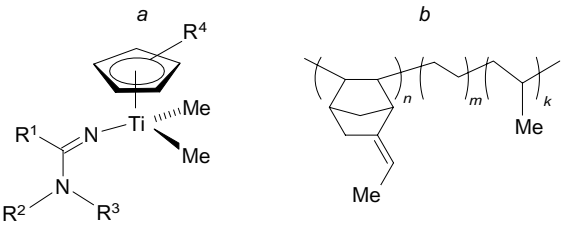
X = Me, Bu^t

copolymerization with methyl acrylate or *tert*-butyl acrylate proceeds in the presence of radical initiators (Scheme 42).[295]

Thus, promising materials for photoresists and highly transparent materials for optoelectronics based on the products of radical copolymerization of norbornene and its derivatives with acrylates have been developed.

5.2.2. Ternary copolymers: ethylene – propylene – diene rubbers

Norbornene derivatives — nonconjugated dienes, dicyclopentadiene, ethylidenenorbornene and vinylnorbornene, — are used in production of EPDM elastomers. These are ternary copolymers of norbornenes with ethylene and propylene. Dienes provide the possibility of vulcanization with sulfur or peroxides. The EPDM material is satisfactorily compartible with fire-resistant hydraulic liquids, ketones, hot and cold water and alkalis. Key properties of EPDM are related to its high resistance to heat, ozone and weathering agents. It is also resistant to the action of polar substances and vapour and exhibits excellent current insulating properties. The EPDM elastomer is used in gaskets, for example, in the doors of refrigeration chambers, face seals of industrial respirators, *etc*. In recent years, ARLANXEO Elastomers has developed Keltan ACE™ technology based on the use of a new class of half-sandwich Ti cyclopentadienyl-1-amidine catalysts (Fig. 24), which are extremely active in manufacturing EPDM.[296]



R^1, R^2, R^3, R^4 = H, Alk

Figure 24. One of the types of Keltan ACE™ catalyst (*a*) and schematic structure of the copolymer of ethylidenenorbornene, ethylene and propylene (EPDM) (*b*).[296]

The developed process makes it possible to produce full assortment of EPDM products with polymer characteristics analogous to those for polymers synthesized in the presence of Ziegler – Natta catalysts. In addition, it provides a high content of 5-ethylidene-2-norbornene and 5-vinyl-2-norbornene in the polymer, controlled branching and high molecular weight.

6. Conclusion

Analysis of the literature data that have appeared in the past 10 – 15 years indicates a significant increase in the interest of chemists in compounds containing norbornene and norbornadiene moieties. The sphere of their use is expanding in the field of producing both strained low-molecular-weight chemically active substrates and new polymeric materials for various purposes. For the optimal solution of the set tasks, available and reliable methods for the selective synthesis of norbornene monomers are necessary. Synthesis of stereoisomeric compounds and materials with optimal structures requires the development of new strategies based on a combination of experimental and theoretical methods and approaches. The presence of feedback between them will make it possible not only to reduce the complexity and optimize experimental studies, but also to better understand the mechanisms of the studied processes. The first steps towards this goal are encouraging, although the researchers will have to overcome many problems, both theoretical and experimental. Along with the undoubted achievements of metal complex catalysis as applied to the chemistry of cage compounds, research has recently begun on the development of heterogeneous catalysts that have technological advantages over homogeneous catalysts.

It has long been known that norbornene derivatives are active and available monomers, but their reactivity decreases or even disappears completely if the monomer contains bulky or highly functionalized groups.[297] It is precisely they that largely determine the chemical value of the target polymer. Therefore, recent studies have focused on the development of ways to synthesize monomers and polymers with properties that are significant for practical use. In particular, such is the witty and practical way of returning high activity to norbornene monomers using the [2 + 2 + 2]-cycloaddition of substituted alkenes to quadricyclane. The resulting tricyclononenes with electronegative substituents remote from the double bond turned out to be more active in metathesis and addition polymerization than norbornene with similar substituents. Significant progress has been achieved in the macromolecular design of polynorbornenes using the metathesis polymerization reaction. The synthesis of highly active catalysts exhibiting stereo- and enantioselectivity, performing living polymerization, thermo- and light-activated, *etc*., makes it possible to involve norbornene with reactive and bulky functional substituents in metathesis polymerization and to synthesize strictly controlled structures with desired properties. The key works dealing with addition polymerization of norbornenes is also devoted to the search for highly active catalysts. The strategy of functionalization of polynorbornene is developed through post-polymerization reactions at the double bonds of the backbone chain of metathesis polynorbornenes or with the participation of side substituents in addition polynorbornenes.

It our opinion, the further development of the chemistry of cage compounds based on norbornene, norbornadiene and quadricyclane should be aimed at searching for and in-depth study of catalytic processes that allow one to regio-, stereo- and enantioselectively carry out the targeted chemical design of low- and high-molecular-weight products of high chemical value.

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