Journal of Organometallic Chemistry, 409 (1991) 15–65
Elsevier Sequoia S.A., Lausanne

JOM 21815REV

Review

SYNTHESIS OF CYCLOBUTANE AND CYCLOPENTANE COMPOUNDS USING HOMOGENEOUS METAL COMPLEX CATALYSTS

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(Received February 22nd, 1991)

CONTENTS

1. INTRODUCTION

Metal complex catalysis is one of the most important tools in the workshop of modern organic chemists. Among the many reactions which it can accomplish are those leading to small rings. Transition metal complexes proved to be extremely effective in bringing about cycloaddition reactions which result in cyclobutanes or cyclopentanes. This unique property of metal complex catalysts results from the very nature of the catalytic action. The central atom of the catalyst is coordinated by several molecules of an unsaturated compound and this favours simultaneous formation of metal-carbon and carbon-carbon bonds resulting in small ring-containing molecules. An important advantage of transient metal complexes is their ability to catalyze symmetry-forbidden cycloaddition reactions.

During the last 15-20 years, many monographs, reviews, and articles have appeared referring to the linear and cyclic oligomerization of olefins, dienes, acetylenes, and allenes under the influence of transient metal complexes. However, there are no reviews so far concerning the application of metal complex catalysts to the synthesis of small ring compounds.

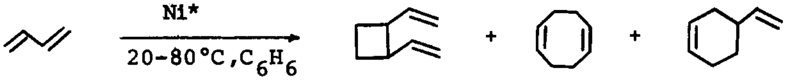
About three years ago a review appeared [1] where the issue of preparing strained polycyclic compounds built from three-, four-, or five-membered rings was discussed. Since then, some important papers were published on the synthesis of cyclobutanes and cyclopentanes from olefins with aid of homogeneous metal complex catalysts.

The rapid development of this area of metal complex catalysis, the appearance of new reactions and synthetic methods, and the practical importance of compounds containing small rings, as well as the lack of reviews stimulated us to write the present paper.

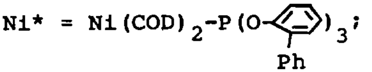
We intend to treat the main achievements in the synthesis of strained cyclobutanes and cyclopentanes by cycloaddition of linear olefins, dienes, allenes, acetylenes, cumulenes, and of "σ-strained" monomers (methylenecyclopropane, cyclopropene, norbornene, norbornadiene and their derivatives) according to the [2 + 1], [2 + 2], [2 + 3], [4 + 2], and [4 + 2 + 2] schemes under the influence of homogeneous metal complex catalysts.

2. CYCLIZATION OF 1,3-DIENES

$[2_\pi + 2_\pi]$ Cyclodimerization of butadiene affording 1,2-divinylcyclobutane (DVCB) (1) is realized on Ni-containing catalysts [2, 3]. The reaction must be carried out in liquid butadiene at incomplete monomer conversion to give DVCB in ca. ~ 40% yield at 85% monomer conversion. The 1,3-diene excess is necessary to prevent Ni(0)-catalyzed DVCB Cope rearrangement into 1,5-cis-cyclooctadiene (COD) [2, 3].

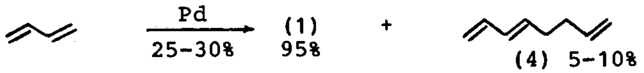


(1) (2) (3)



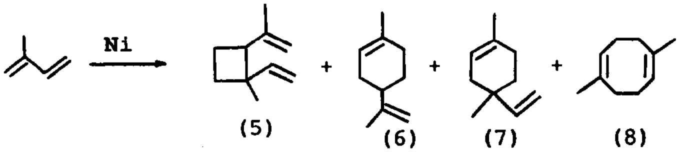
Ni* = $Ni(COD)_2$-$P(O$-$C_6H_4Ph)_3$; $Ni(acac)_2$-$P(OR)_3$-$AlEt_2(OEt)$

Catalysts based on palladium compounds demonstrate higher selectivity (ca. ~95%) for DVCB [4, 5]. $Pd(ClO_4)_2$, $Pd(BF_4)_2$, Or $Pd(OAc)_2$ deposited on styrene and divinylbenzene copolymer convert butadiene at 90°C during 10 hrs into a mixture of the two dimers DVCB and 1,3,7-octadiene (4). The disadvantage of the Pd-containing catalyst is the low total yield of (1, 4) (ca. ~ 25-30%).



(4) 5-10%

Complexes of Ni(0) induce the [$2\pi + 2\pi$] cyclodimerization of 1- and 2-substituted 1,3-dienes [6-11]. Isoprene predominantly forms the cyclobutane isomer (5), one of six possible structures.



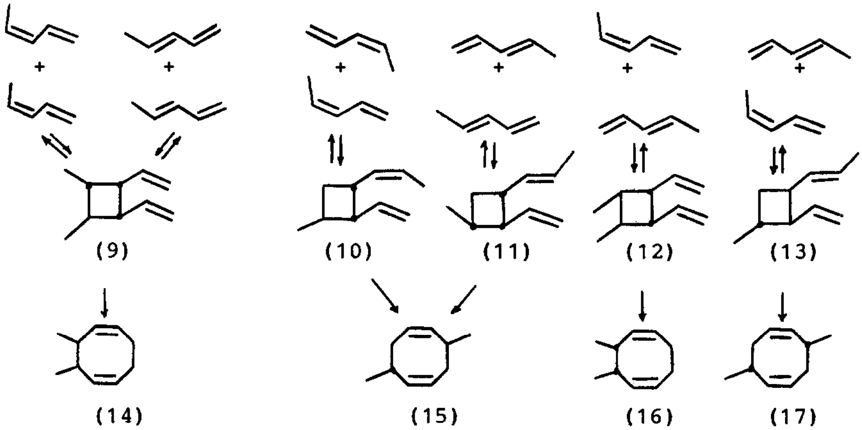
(5) 12-15%   (6)   (7)   (8)

Despite low yields (12-15%), this approach to hydrocarbon (5) is of preparative value. Compound (5) has been successfully converted into (±)-grandizole, the main component of the sex pheromone of male boll weevil [7].

The formation of divinylcyclobutane (9-13) via [$2\pi + 2\pi$] cyclodimerization of Z- and E-piperylenes is interesting from the theoretical point od view. As is seen in Scheme 1, the product mixture is rather complex.

Using $Ni(COD)_2$-L [L = tris(o-phenylphenyl)phosphite, $P(OPh)_3$, $P(C_6H_{11})_3$] catalyst at 30°C afforded 16-92% yields of (9-17). This reaction leads to five cyclobutane isomers (9-13) together with isomeric dimethylcyclooctadienes (14-17).

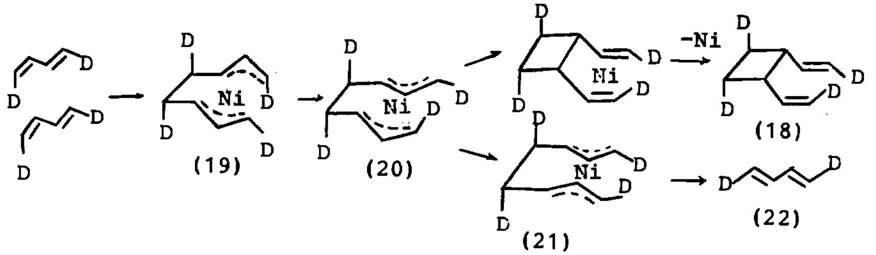
Scheme 1.



The overall yield and isomeric composition of the products (9-17), isolated and spectroscopically identified, depend on the nature of the ligand as well as on the starting monomer conversion and the geometry [8]. Detailed studies into the composition of the starting and final products enabled the authors to make important conclusions regarding the 1,3-diene cyclodimerization mechanism. The thermodynamic equilibrium between Z- and E-piperylenes and divinylcyclobutanes has been identified [8, 11] (Scheme 1). Simultaneously, Z-piperylene isomerizes into the E-form via decomposition of cyclobutane derivatives (9, 10).

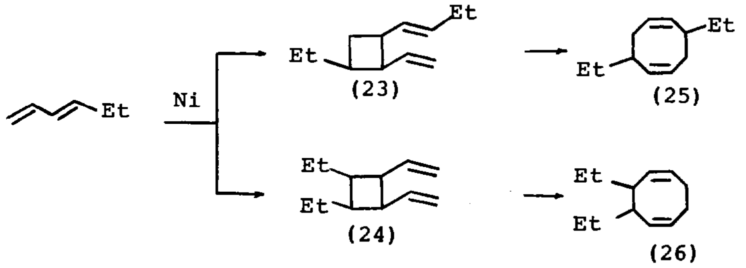
Both the geometrical isomerization of piperylene and the reversibility of the (9-13) $\rightleftharpoons$ Z- and E-diene reaction are assumed to support the stepwise mechanism of $[2_\pi + 2_\pi]$-cyclodimer formation from 1,3-dienes which most probably involves σ-, π -, or π-allyl intermediates.

Later this conclusion was proved by the authors of communication [12] who found that the the cyclodimerization of cis-1,4-dideuteriobutadiene-1,3 into DVCB carried out in benzene at 20°C in the presence of the catalytic system $Ni(COD)_2$-PPh_3 involved several steps and included the formation of the anti-π-allylic complex (19) which transformed into the syn-π-allylic complex (20) via π-allylic intermediates. The reaction was completed by intramolecular reductive elimination of Ni(O) to lead to DVCB (18).

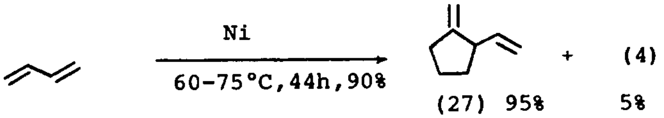


Simultaneous rapid isomerization of 1,4-cis-dideuteriobutadiene-1,3 into the trans-isomer (22) occurred via complex (21).

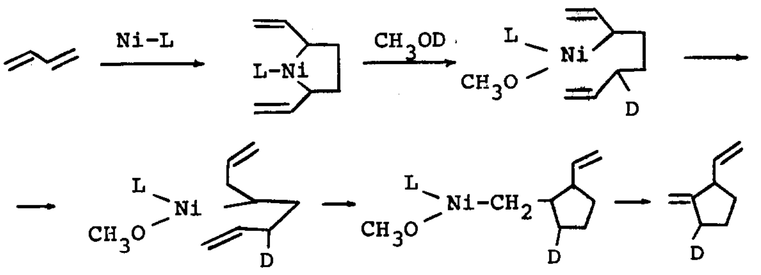
E-1,3-Hexadiene could also be caused to undergo $[2_\pi + 2_\pi]$ cyclodimerization [11]:



In 1970 Japanese researchers [13-16] accomplished the cyclization of butadiene into 1-vinyl-2-methylenecyclopentane (27).



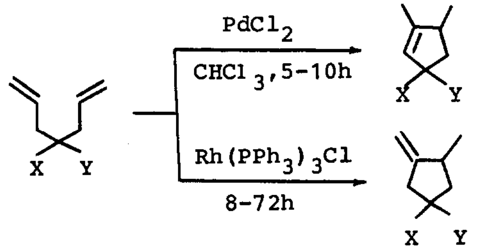
This reaction is carried out with Ni-containing catalysts of general formula $R_3P \cdot NiX_2$ (where R_3P = tributylphosphine, triphenylphosphine, or diethylphenylphosphine; X = Cl, Br) reduced by $NaBH_4$, BuLi, MeONa, or N,N-dimethylbenzoamino-o-lithium in equimolar amounts and in the presence of an aliphatic alcohol, preferably methanol [13-15]. The optimal methanol:butadiene ratio for high selectivity (up to 95%) and high yield of (27) ranges between 1:2 and 1:3. On change of MeOH for MeOD half amount of (27) was deuterated. According to PMR and mass-spectral data, most of the deuterium in (27) is localized at the C-3 atom. The formation of the partially deuteriated cyclodimer (27)-D suggests the direct participation of methanol in the catalytic process as follows [13, 14]:



(27)-D_1

Substituted 1,3-dienes do not undergo the reaction.

Cyclopentanes can also be obtained by intramolecular cyclization of 1,6-dienes under the influence of Pd- or Rh-containing catalysts [17, 18]:

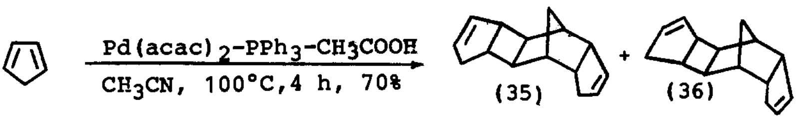


X = Y = COMe (28)
CO_2Et (29)
COPh (30)

X = CO_2Et, Y = COMe (31)
X = Y = COMe (32)
CO_2Et (33)
COPh (34)

Under the same conditions, 4-oxa- or 4-aza-1,6-dienes form furane, pyrroline or pyrrolidine derivatives [19-21].

As to cyclic 1,3-dienes, the $[2_\pi + 2_\pi]$ cycloaddition catalyzed by transition metal complexes and leading to the formation of small rings is not common for these species. The trimerization of cyclopentadiene upon Pd-containing catalysts promoted by by carboxylic acids (pK_a = 3-5) (Pd/acid = 1/500) is the only case reported elsewhere [22].



(35) (36)

The reaction has not been studied in detail, but one cannot exclude the formation of endo-dicyclopentadiene as being the initial step.

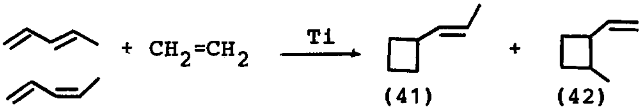
2.1. Cycloaddition of 1,3-Dienes to Linear Olefins according to the $[2_\pi + 2_\pi]$ Scheme

Cycloaddition of butadiene to ethylene , according to the $[2_\pi + 2_\pi]$ scheme, occurs under the action of titanium-containing catalysts [22-28]. Of the highest reactivity are Ti complexes $Ti(CH_2Ph)_4$, $(C_5H_5)Ti(CH_2Ph)_3$, and Ziegler type catalysts $(C_5H_5)TiCl_3$-$AlEt_3$ and $(n\text{-}BuO)_4Ti$-$AlEt_3$ [23-25].

(37) (38) (39) (40)

The severe conditions of this reaction probably cause the low selectivity. The interaction of Lewis bases (e.g. 2,2'-dipyridyl or 1,10-phenanthroline) with the Ti complex catalyst tends to increase the selectivity [23-25]. The change of the aromatic solvent for one of the ether type (THF) gives similar results. The best yield of VCB (37) is ca.~44% [23-25]. The search for active catalysts for cycloadditioning butadiene to ethylene has been continued [26-28]. With the aim of enhancing the catalyst selectivity for vinylcyclobutane, the authors of [25-27] have tested Ti complexes containing anions [$(CH_3)_3SiO$-, $(CH_3)_3Si$-CH_2-] etc., or neutral ligands (PPh_3) and have changed the pyrophoric reductant $AlEt_3$ for organomagnesium compounds. Thus, using the $(C_5H_5)Ti[O\text{-}Si(CH_3)_3]_3$ complex they achieved 65% selectivity for VCB, the total yield of the co-dimers (37-40) being 85% [26-28]. The catalyst $(C_5H_5)TiCl_2Br(CH_3)_3SiCH_2MgCl$ has still higher selectivity for VCB (72%). The monocomponent catalysts $(C_5H_5)Ti[CH_2\text{-}Si(CH_3)_3]_3$ or $Ti[O\text{-}Si(CH_3)_3]_4$ prove to have a low activity. On addition of neutral ligands (PPh_3, 2,2-dipyridyl) to the $Ti[OSi(CH_3)_3]_4$-$AlEt_3$ system the reaction slows down strongly though the selectivity for VCB increases to 80% [28].

Z- and E-Piperylenes take part in the [$2_\pi + 2_\pi$] cycloaddition to ethylene [23-25, 28].

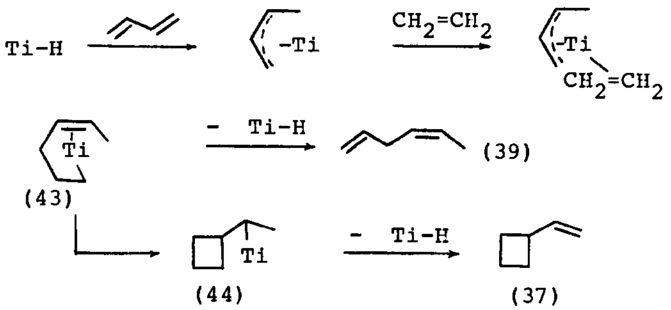


(41) (42)

48% trans
9% cis

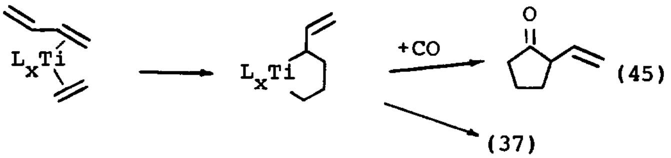
Under the same conditions, isoprene and ethylene form linear codimers only [26].

Several hypotheses have been published **concerning** the mechanism of 1,3-diene cycloaddition to ethylene under the influence of Ti complexes. Cannell who was the first investigator of the interaction between ethylene and butadiene, offers a scheme based on traditional ideas of homogeneous metal complex catalysis [23, 25]:



The scheme proposes the formation of a common σ-hexenyl intermediatory complex (43) for both the linear codimer (1,4-hexadiene) and the cyclic one (VCB). The reaction may follow two directions, both involving titanium hydride β-elimination. To explain the formation of VCB, Cannell assumes an additional step of intramolecular carbotitanation of a double bond leading to the cycloalkyl complex (44). However, this hypothesis is not supported by experiment and it cannot rationalize the high selectivity of the reaction for vinylcyclobutane.

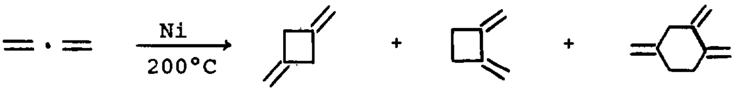
The author of an alternative model for the formation of VCB [28] demonstrated carbonylation of a reaction mixture containing butadiene, ethylene, and the catalytic system $(C_5H_5)TiCl_3$-lithium naphthalide and isolated 2-vinylcyclopentanone (45) in 14%yield. Further, experiments on cyclodimerization of D_6-butadiene and ethylene in the presence of $(C_5H_5)Ti[OSi(CH_3)_3]$-CH_3MgI as catalyst led to essentially pure D_6-VCB. This result excludes hydride shift and the formation of intermediate Ti-H (or Ti-D) complexes. Based on these data, a mechanism is proposed which involves the key step of the formation of a metallocyclopentane (46) [28]:



This correlates well with the results of quantum mechanical calculations performed by R.Hoffmann et al.[29] who have noted the preferential formation of metallocyclopentane in these reactions through the synchronous oxidative addition of butadiene and ethylene molecules coordinated to the central metal atom.

3. CYCLOOLIGOMERIZATION OF ALLENES, ACETYLENES, OR CUMULENES LEADING TO STRAINED RINGS

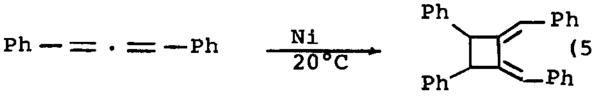
Compounds containing strained small rings can be obtained by cyclization of 1,2-dienes under the influence of transient metal complexes. Cyclodimerization of the simpliest 1,2-diene, allene, into 1,3- and 1,2-dimethylenecyclobutanes with a catalyst $[Ph_2P(CH_2)_2PPh_2]\cdot Ni(CO)_2$ has been described [30]. Carrying out the reaction at 200°C in gaseous phase affords dimers (47, 48) together with trimeric 1,2,4-trimethylenecyclohexane (49), the total yield amounting to ca.$\sim$73% and the allene conversion being ca. 61%.



(47) 60% (48) 13% (49) 27%

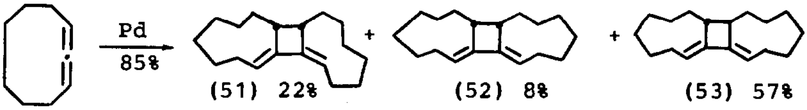
Changing the bidentate bis-phosphine ligand in the Ni catalyst to PPh_3 reduces selectivity for dimers to 15% and increases the content of trimer (49). In the liquid phase (THF soln) the reaction is directed towards tetramers, pentamers and higher oligomers of allene [29].

Unlike propadiene-1,2, 1,3-diphenylallene gives only the 1,2-isomer (50) under the influence of $(C_5H_5)_2Ni\text{-}P(OEt)_3$ catalyst [31].



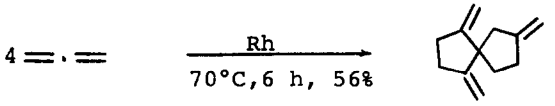
(50)

An example of $[2_\pi + 2_\pi]$ cyclodimerization of a more complex allene, 1,2-cyclononadiene, is known [32]. Studies of the cooligomerization of the latter and methylenecyclopropane (MCP) have shown that most of the cyclic allene is converted into a mixture of cyclobutane derivatives (51-53):



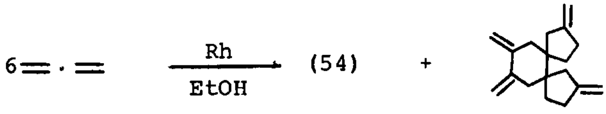
(51) 22% (52) 8% (53) 57%

The action of rhodium complexes leads to unexpected catalytic transformations of allene into spiro-conjuncted strained hydrocarbons [33-35]. Thus, on heating allene at 70°C for 6 hrs in the presence of $Rh(PPh_3)_3Cl$ or $Rh(CO)(PPh_3)_2Cl$ complexes in chloroform solution, the spirocyclic tetramer (54) has been prepared in a 56% yield.



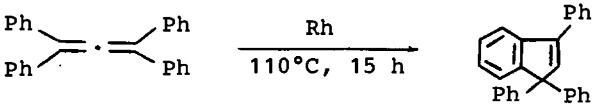
(54)

The yield of the tetramer has been increased to 70-80% by using the $Rh_2Cl_2(C_2H_4)_2$ complex activated by two moles of PPh_3 in ethanol [34, 35]. The cyclodimerization of allene with a $Rh(CO)_2Cl_2$-PPh_3 catalyst results in the dispiro-hexamer (55) together with the tetramer (54) [36].



(55)

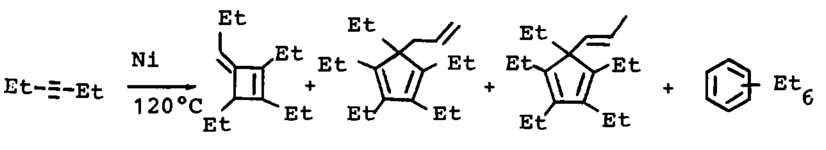
The transformations described here are unknown for substituted 1,2-dienes. For example, 1,1,3,3-tetraphenylallene on heating in the presence of Wilkinson's complex $Rh(PPh_3)_3Cl$, undergoes isomerization into 1,3,3-triphenylindene (56) [33].



(56) 24%

Complexes of Ni enabled cyclooligomerization of acetylenes to give 4- and 5-membered cycles [37].

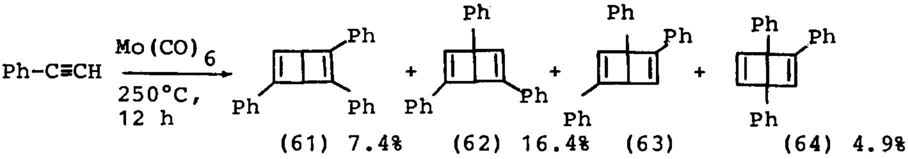
Thus hexyne-3 on heating in benzene in the presence of $[H\text{-}Ni(diphos)_2]OCOCF_3$ is converted into a hydrocarbon mixture consisting of dimer (57) and trimers (58-60), the yield of cyclobutane derivative ammounting to ca.$\sim$36%.

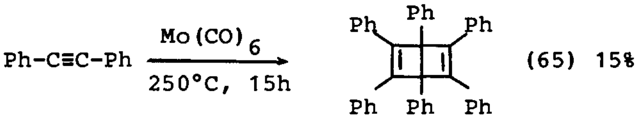


(57) (58) (59) (60)

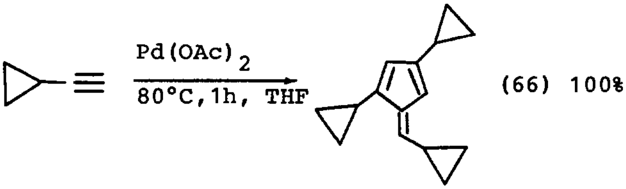
If the Ni-hydride complex is changed for $Ni(COD)_2$-$4PPh_3$ and the reaction is carried out under gaseous CO_2, trimers (58 and 59) are formed predominantly [37].

Recently an unusual reaction was reported for the double homo $[2\pi + 2\pi]$ cycloaddition of phenyl- and diphenyl-acetylenes under the influence of $Mo(CO)_6$ giving substituted derivatives of Dewar benzene [38, 39].



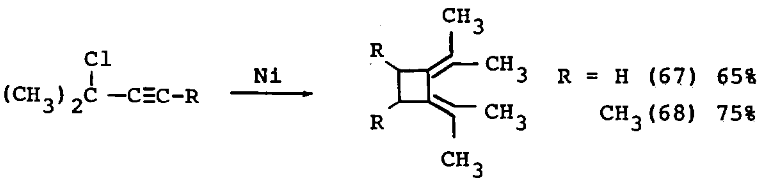


Cyclopropylacetylene undergoes an unusual catalytic cyclization [40].

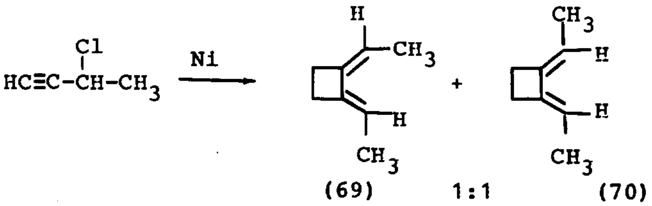


Phenylacetylene also undergoes a similar reaction in the presence of the $Pd(Al_3Cl_7)_2 \cdot 2C_6H_6$ binuclear complex [41].

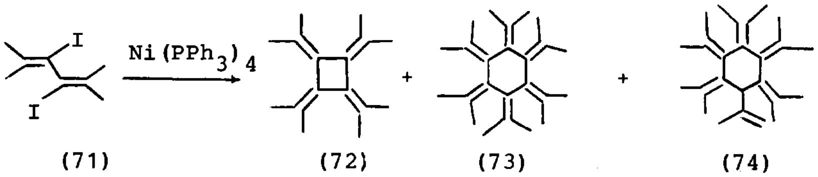
Under the action of the zero-valent Ni complex $Ni(PPh_3)_4$, 3-halogenoacetylenes cyclize into 3,4-dimethylenecyclobuten-1 derivatives [42]. This complex reaction comprises an intramolecular dechlorination step. The catalyst here serves also as a halogen acceptor, and hence a nearly stoichiometric amount of the Ni° complex is necessary; the molar ratio of Ni° to 3-halogenoacetylene is 1:5.



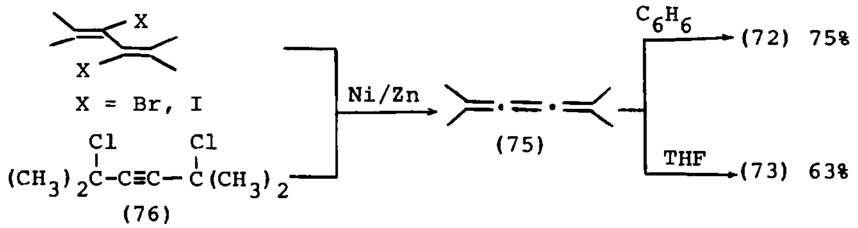
3-Chloro-1-butyne reacts similarly [42].



The ability of zero-valent Ni complexes to cause simultaneous dehalogenation and cyclization has been used in elegant synthesis of 4- and 6-radialenes [43, 44].

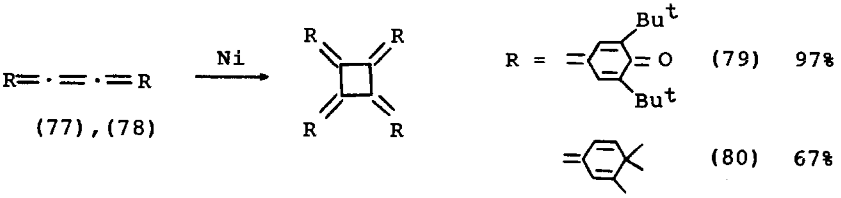


The structure of isopropylidenecyclanes (72-74) suggests that the cyclization is preceeded by dehalogenation of 3,4-diiodo-2,5-dimethylhexadiene (71) into 1,1,4,4-tetramethylbutatriene (75). The isomeric composition of the products is dependent upon the nature of solvent, and maximum selectivity for the cyclobutane isomer (72) is observed in benzene solution [43]. If metallic zinc is used as the dehalogenation agent together with Ni$(PPh_3)_4$, the yield of (72) is increased to 75%, and the starting compound (71) can be replaced by the readily available 5,6-dichloro-2,5-dimethylhexyne-3 (76) [44].



The cyclobutane dimer (72) has been directly obtained from 1,1,4,4-tetramethylbutatriene [45].

Dimerization of stable cumulenes (77, 78) into the corresponding cyclobutane derivatives proceeds smoothly, with high selectivity and in good yields if carried out in the presence of Ni$(PPh_3)_2(CO)_2$ [46, 47].

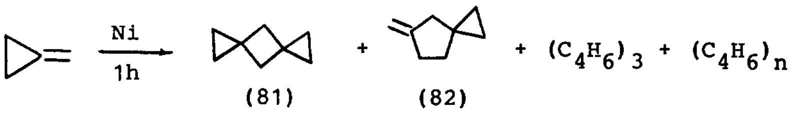


4. CYCLOOLIGOMERIZATION OF "σ-STRAINED" MONOMERS

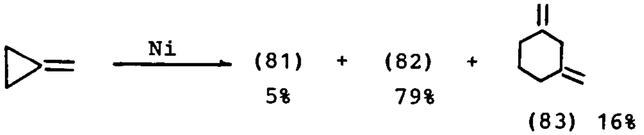
4.1. Cyclization of Methylenecyclopropanes

The homooligomerization of methylenecyclopropane (MCP) and its substituted derivatives under the influence of metal complex catalysts is of special interest because it paves a smooth and easy way to poorly available polycyclic compounds of spirane structure.

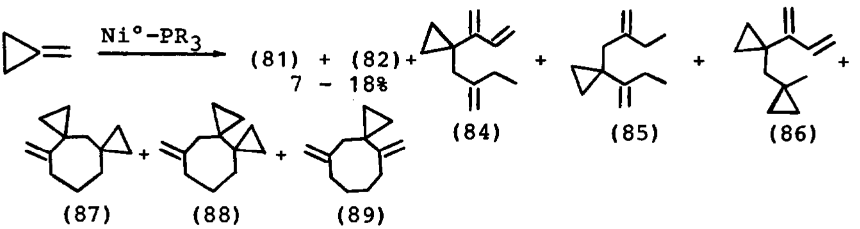
The exothermic catalytic homooligomerization of methylenecyclopropane in the presence of Ni(COD)$_2$ commences at -15°C and gives two isomeric dimers (81, 82) (total yield 45%) as well as trimers (10%) and higher oligomers of unidentified structure (MW 1.100, ca.∼45%) [48, 49].



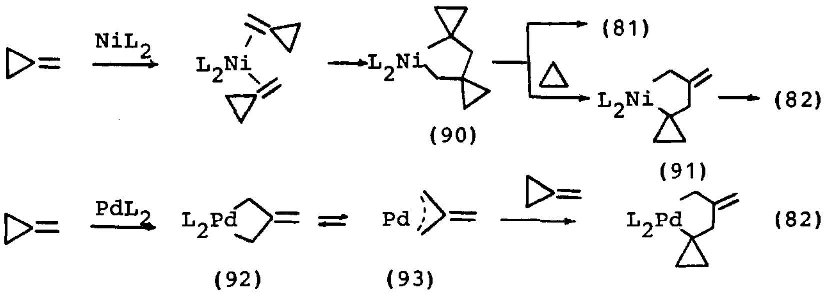
The introduction of maleic anhydride (MA) into the catalyst [Ni(COD)$_2$: MA = 1:10] results in 97% selectivity for 3-methylene-spiro[4.2]heptane (82) [50]. On using dimethyl, diethyl, or dibutyl fumarates as the solvent, another dimer, mainly 1,3-dimethylenecyclohexane (83) has been found [50].



The addition of organophosphorous activating agents to the Ni-containing catalyst favours the formation of MCP trimers (84-89) the total yield of which can reach ca. 93% [51].

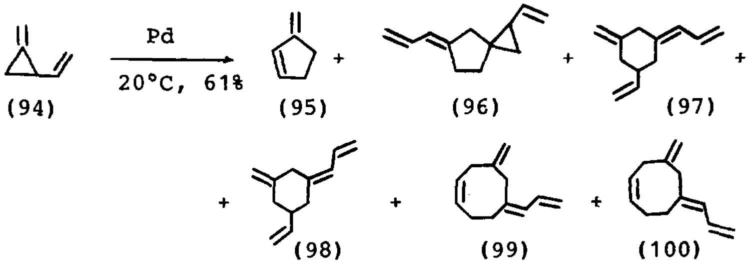


Unlike Ni catalysts, those based on Pd: Pd(acac)$_2$-P(i-Pr)$_3$-AlEt$_2$(OEt) or Pd$_2$(DBA)$_3$- P(i-Pr)$_3$, bring about selective MCP dimerization into 3-methylene-spiro[4.2]heptane (82) [32]. The difference in selectivity between Ni and Pd catalysts is associated with a change in the reaction mechanisms [32, 52].

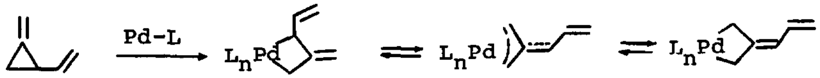


As is seen from the above scheme, Pd-catalyzed cycloaddition begins with the rupture of the C_3-C_4 bond in the three-membered ring, while under the action of Ni° complexes, opening of the ring, which is known as "cyclopropyl-3-butenyl rearrangement" occurs only during the third step. Hence, different paths lead to one and the same dimer (82) with Ni and with Pd. The presence of Ni° ensures the predominance of $[2\pi + 2\pi]$ cycloaddition, while Pd° complexes exclusively cause $[3\pi + 2\pi]$ cyclization. The different ways of MCP reacting in the presence of Pd° and Ni° complexes are supported by the structure of intermediate complexes (90, 91) which could be isolated and identified [32, 52].

1-Methylene-2-vinylcyclopropane (94) is the only substituted cyclopropane capable of entering the homodimerization [53] which is catalyzed by Pd complexes and proceeds according to the $[3\pi + 2\pi]$ cycloaddition scheme. Some monomers such as (94) undergo isomerization into 3-methylene-1-cyclopentene (95) in the course of this reaction.



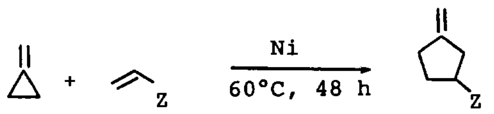
The unususal structure of dimers (96-100) has been explained by the existence of the following equilibrium [53]:



There are no other examples of the homodimerization of substituted methylenecyclopropanes.

4.2. Cycloaddition of Methylenecyclopropanes to Linear Olefins

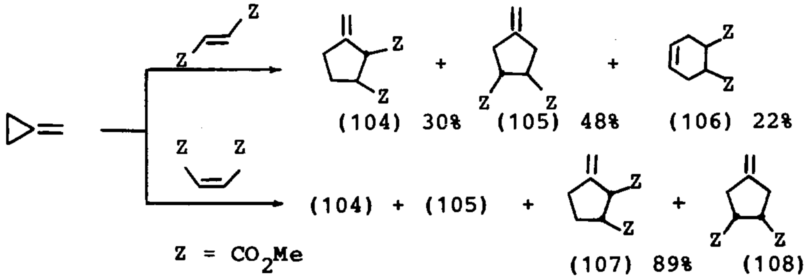
Unlike homooligomerization of methylenecyclopropane and some analogues of this, which could be carried out in some particular cases only, cyclodimerization of these monomers with unsaturated compounds, which is essentially $[3\pi + 2\pi]$ cycloaddition, is a more common reaction. Catalyzed by Ni or Pd complexes, it is of considerable synthetic importance affording cyclopentane derivatives. Methylenecyclopropane $[3\pi + 2\pi]$ cycloaddition proceeds more easily to activated olefins. This transformation has been studied for methylenecyclopropane and acrylic monomers using a Ni-acrylonitrile complex catalyst [54].



Z = CO_2Me (101)
COMe (102)
CN (103)

It was found later that the $Ni(COD)_2$ complex is a more effective catalyst; the codimerization of methylenecyclopropane and methylacrylate occurs in only 5 hrs in a ca. ~90% yield [55]. The catalyst remain active even at temperatures below 0°C. In the presence of $Ni(COD)_2$, $[3\pi + 2\pi]$ cycloaddition of MCP to chiral acrylic esters such as (-)-bornyl, (-)-menthyl, or (-)-phenylmenthyl acrylates can proceed with asymmetric induction [56]. Between -20°C and +40°C the codimer yields amount to 80-90%. The optical yield between -20°C and -25°C is essentially constant at ca. ~64%. At>25°C the optical yield diminishes to 3%.

The codimerization of methylenecyclopropane with 1,2-disubstituted olefins under the influence of Ni complexes is non-selective and leads to a mixture of 2,3- and 3,4-disubstituted 1-methylenecyclopentanes [50, 57, 58].



(104) 30% (105) 48% (106) 22%

(107) 89% (108) 6%

Z = CO_2Me

The ratio of the 2,3- and 3,4-isomers depends to some extent on the composition of Ni-containing catalyst but mainly on the olefin substituent. Thus, a high selectivity for 2,3-isomers in the presence of Ni(COD)$_2$-PPh$_3$ catalyst has been found for olefins containing a single electron-acceptor substituent [59].

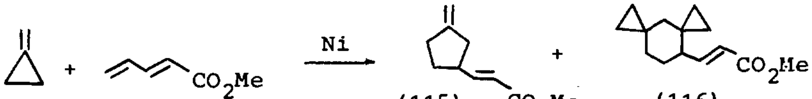
R = H Z = CO$_2$Me (101) 55%
cis/trans = 22/78
CH$_3$ (E) CO$_2$Me (109) 55%
cis/trans = 27/73

R = C$_3$H$_7$ (E) Z = CO$_2$Me (110) 50%
(cis/trans/ 27/73)
(CH$_2$)CO$_2$Me (E) CO$_2$Me (111) 49%
(cis/trans = 28/72)
CH$_3$ CHO (112) 54%
(cis/trans = 9/91)

Olefins with two such substituents form 3,4-cyclodimers under the same conditions [59].

Z = CO$_2$Et (E) (113) 72% (cis/trans = 4/96)
CO$_2$Et (Z) (114) 42% (cis/trans = 25/75)

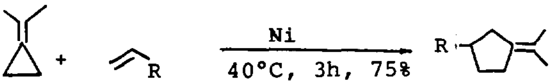
The interaction between MCP and the methyl ester of butadienecarboxylic acid with Ni(COD)$_2$ is peculiar in that it involves exclusively the diene vinyl group [60].



(115) (116)

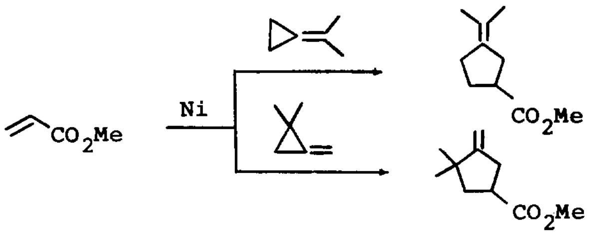
Along with the known [3$_\pi$ + 2$_\pi$] cycloaddition a novel noteworthy direction is realized here, cyclotrimerization leading to the unusual product (116).

The nature and location of a substituent in MCP strongly affect the course of the cyclodimerization. Thus, isopropylidenecyclopropane with Ni(COD)$_2$ reacts with ethylene as well as with styrene.



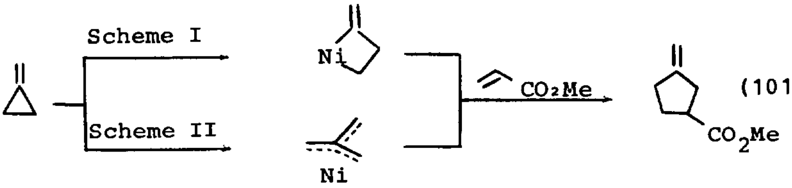
R = H (117)
Ph (118)

The Ni(CH$_2$=CH-CN)$_2$ complex catalyzes [3$_\pi$ + 2$_\pi$] cycloaddition of isopropylidenecyclopropane and 2,2-dimethyl-1-methylenecyclopropane to methyl acrylate [54].



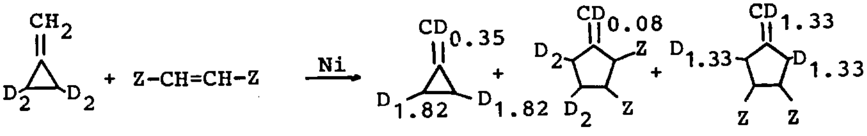
(119)
(120)

Having analyzed possible ways for the formation of codimers (119, 120), the authors of [57, 58] offer two alternative schemes for the cycloaddition of MCP to methylacrylate.



(121)
(101)

Taking into account the structure of (119), R.Noyori et al. prefer the first scheme and exclude the pathway via the Ni-trimethylenemethane complex (121) (Scheme II). It should be noted, however, that both pathways for the reaction have been reported. This may be illustrated by the interaction between partially deuterated MCP (122) and dimethyl esters of fumaric and maleic acids [58].

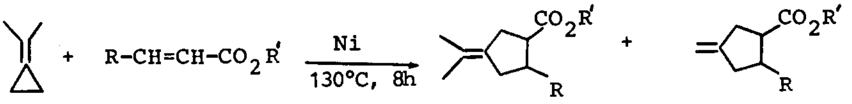


(122)
(123)
(124)
(125)

$Z = CO_2Me$

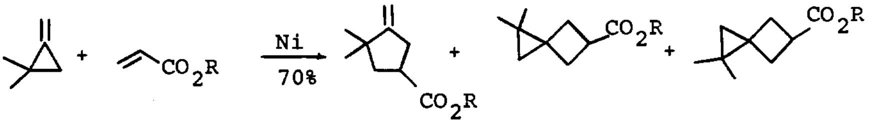
The observed purely statistical distribution of deuterium in the methylcyclopropane moiety of hydrocarbon (125) can arise only if all the three methylene groups become equivalent after the rupture of the MCP C-C bond by the central catalyst atom, i.e. if the reaction proceeds via complex (121). Hence, codimer (125) is most probably formed according to Scheme (II), while (124) is the product of Scheme (I).

The structure of the products proves that both pathways are realized also in the cycloaddition of isopropylidenecyclopropane to acrylic, fumaric, and maleic acid derivatives in the presence of Ni(COD)$_2$ or Ni(1,5,9-CDT) (CDT = cyclododecatriene) activated by aryl phosphites [61].



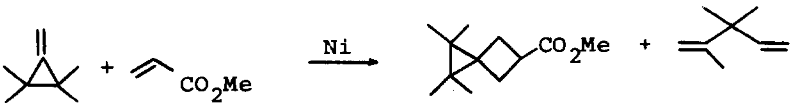
R = H	R' = CH$_3$	(126) 81%	(127) 14%
CH$_3$(E)	CH$_3$	(128) 14%	(129) 46%
CO$_2$Et (E)	C$_2$H$_5$	(130) 56%	(131) 34%
CO$_2$Et (Z)	C$_2$H$_5$	(132) 57%	(133) 23%

Of special interest are the results obtained for codimerization of acrylic acid esters and 2,2-dimethyl-1-methylenecyclopropanes under the influence of Ni(COD)$_2$ [55].



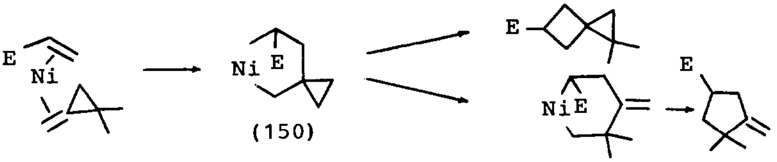
R = CH$_3$	(127) 82%	(138) 6%	(143) 12%
C$_2$H$_5$	(134) 78%	(139) 7%	(144) 15%
i-C$_3$H$_7$	(135) 74%	(140) 8%	(145) 18%
n-C$_4$H$_9$	(136) 77%	(141) 8%	(146) 15%
t-C$_4$H$_9$	(137) 60%	(142) 9%	(147) 31%

As is seen from the above scheme, the cycloaddition of 2,2-dimethyl-1-methylenecyclopropane to acrylates follows $[3\pi + 2\pi]$ and $[2\pi + 2\pi]$ paths, the contribution of the latter increasing with the degree of spatial hindrance in the olefin ester group. Under the same conditions $[2\pi + 2\pi]$ cyclodimerization becomes the sole mode of reaction in the interaction between 2,2,3,3-tetramethyl-1-methylenecyclopropane and methyl acrylate.

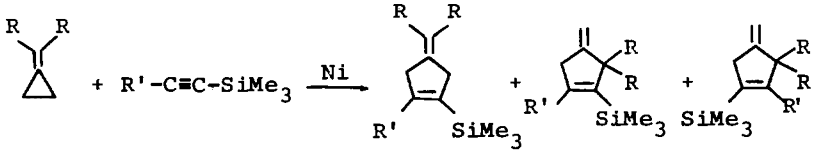


(148) 75% (149) 14%

The authors of [55] have put forward proposals regarding the main steps of catalytic reactions involving MCP [28, 43] and its derivatives. They ascribe the increase in the proportion of $[2\pi + 2\pi]$ codimers to the diminution of the contribution of "cyclopropyl-3-butenyl rearrangement" in the intermediatory Ni-cyclopentane complex (150) because of the increased rigidity of the three-membered ring due to the presence of methyl groups, and because of steric hindrance connected with the presence of substituents both in MCP and in olefin ester group.

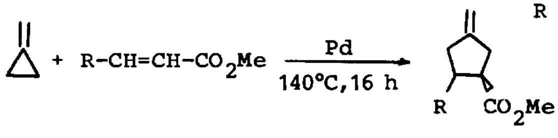


Acetylenes as well as activated olefins may take part in $[3_{\pi} + 2_{\pi}]$ cyclocodimerization with alkyl- or phenylsubstituted methylenecyclopropanes [62]. The reaction proceeds with $Ni(COD)_2$-tris(o-biphenyl) phosphine catalyst for 5-8 hrs at 80°C. The presence of at least one α-trimethylsilyl group in the acetylenic substrate is necessary. The nature of the other substituent at the triple bond is important in determining the isomeric composition of the codimers (151-184). Yields amount to 90-95% on alkyne consumed. Mono- and di-alkylacetylenes are predominantly converted into cyclotrimers and tetramers.



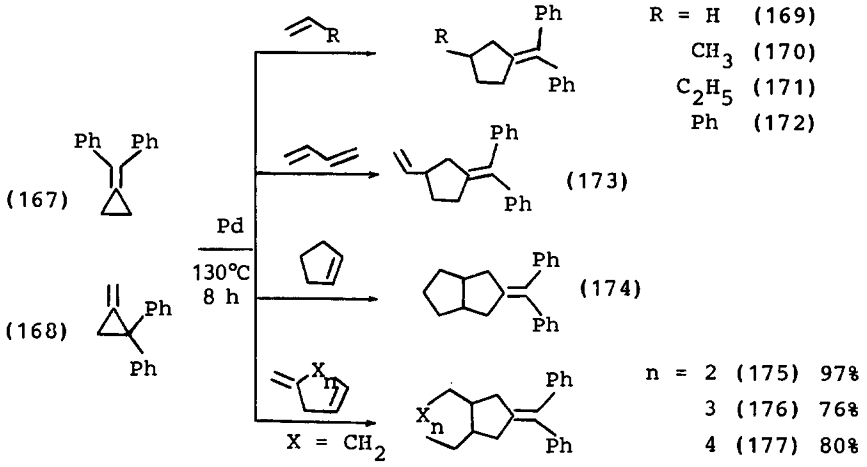
R = H, R = C_5H_{11},	R' = CH_3	(151) 12%	(152) 63%	(153) 25%
R = R = CH_3	$SiMe_3$	-	(154) 63%	-
Ph	C_2H_5	(155) 60%	(156) 24%	(157) 16%
Ph	CO_2Me	(158) 100%		
CH_3	CH_2OSiMe_3	(159) 6%	(160)	(161) 34%
Ph	CH_2OSiMe_3	(162) 63%	(163) 2%	(164) 45%

Pd-Based catalysts are quite effective for the $[3_{\pi} + 2_{\pi}]$ cycloaddition of methylenecyclopropanes to activated olefins, and are highly selective for the formation of 3,4-codimers [32,63].



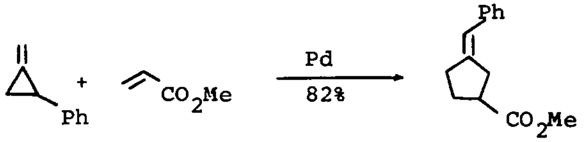
R = H		(101)	80%
CH_3		(165)	42%
Ph		(166)	14%
CO_2Me	(E)	(108)	57%
CO_2Me	(Z)		78%

Another important feature of complex Pd catalysts is their ability to cause methylenecyclopropanes to add to inactivated or poorly activated olefins [64].



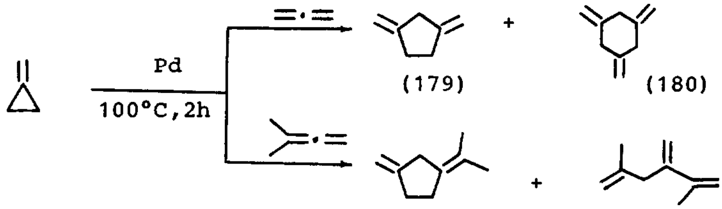
The above examples show that when Pd complexes are used as catalysts, the regioselectivity does not depend on the structure of the methylenecyclopropane. For example, both 1,1-diphenylenecyclopropane (167) and 2,2-diphenyl-1-methylenecyclopropane (168) form identical products (169–177) on codimerization with olefins.

In the same way, 1-methylene-2-phenylcyclopropane reacts with methyl acrylate to give a single regioisomer with a phenyl group positioned at the exocyclic methylene carbon atom [65].



(178)

$[3_{\pi} + 2_{\pi}]$ Cycloaddition of MCP to 1,2-dienes has been carried out with the aid of Pd complexes [32].

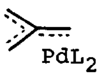


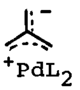
(179) (180)

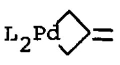
(181) (182)

4.3. Cycloaddition of Methylenecyclopropane Synthetic Equivalents

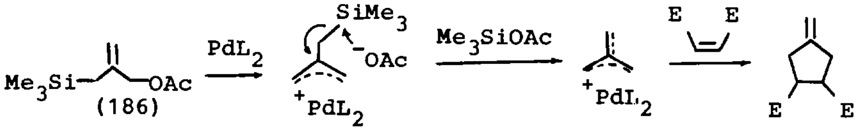
As follows from the previous section, $[3_{\pi} + 2_{\pi}]$ cycloaddition of MCP to a double bond may provide an effective method of planned cyclopentanoid synthesis. However, this has the serious shortcoming in that the formation of a five-membered ring is achieved by the opening of a three-membered one which is even less available . One of the possible ways to overcome this difficulty has been found by Trost in his analysis of the reaction mechanism. It is evident that the catalytic cycle of the $[3_\pi + 2_\pi]$ cycloaddition of MCP to olefins involves rupture of the three-membered ring. Despite abundant evidence concerning the key role in the process of the Pd complexes, the structure of intermediates in these reactions has not been firmly established. Three types of active molecules are considered most probable, i.e. an η^4-coordinated trimethylenemethane (183) complex, an η^3-coordinated polar one (184), and a palladiacyclobutane (185) molecule.


(183)


(184)


(185)

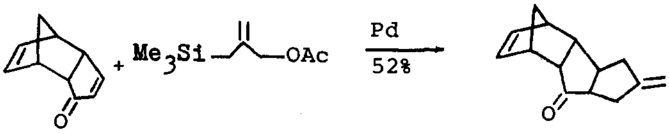
If a complex (183-185) is involved in the formation of a five-membered ring, the products should not depend on the source of the complex. Trost has found a suitable compound which is able to generate complexes (183-185) and represents an open-chain molecule [66]. It appears that (2-trimethylsilylmethyl)allyl acetate (186), in the presence of Pd complexes, becomes a synthetic equivalent of MCP or, to be more exact, of trimethylenemethane.


(186)

In this reaction, the central atom of the metal performs a set of important functions. It catalyzes the rupture of Si-C and C-O bonds thus enabling the main catalytic process. The leaving groups, $SiMe_3^+$ and AcO^-, are eliminated as a neutral Me_3SiOAc molecule while the trimethylenemethane moiety adds to the double bond. This transformation sequence can be catalyzed only by zerovalent Pd complexes with tertiary phosphine additives. The $Pd:PR'_3$ molar ratio is of crucial importance for the reaction ranging between 1:2 and 1:4 [66-69]. The ligand excess is particularly necessary to augment the catalyst stability because both starting compounds and the by-product Me_3SiOAc are polar species and can compete with phosphines at the coordination site at Pd atom.

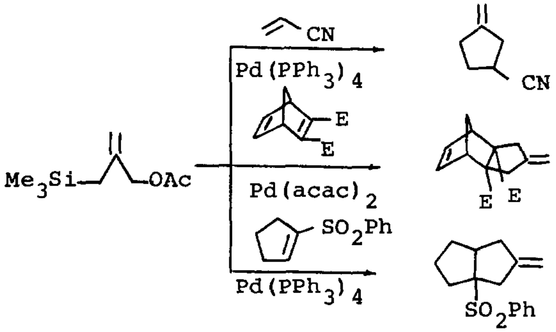
However, MCP does not require this and readily enters $[3_\pi + 2_\pi]$ cycloaddition to olefins at equimolar Pd:PR$_3$ ratio.

Another peculiarity of Trost's method is represented by its high selectivity. This is well supported by the following example:



(187)

The direction of trimethylenemethane attack is determined by the structure of the starting olefin. The presence of an electron accepting α-substituent (carbonyl, ester, nitrile, or sulphonyl) is a necessary and sufficient condition for the $[3_\pi + 2_\pi]$ addition of trimethylenemethane [67, 69].

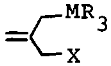


(103)

(188)

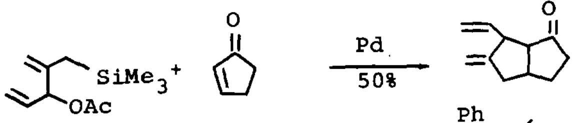
(189)

The list of trimethylenemethane synthetic equivalents has subsequently been considerably increased [70-74]:



MR_3 = SnMe$_3$, SnBu$_3$; X = $\mathrm{O{-}\underset{\displaystyle O}{\overset{}{\underset{\|}{C}}}{-}OMe}$, $\mathrm{O{-}\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}}{-}CH_3}$, I

Several modifications are known which are useful in synthesis For example, introduction of geminal substituents into (2-trimethylsilylmethylene)allyl acetate molecule makes possible the preparation of 2-substituted methylenecyclopentanes [71].



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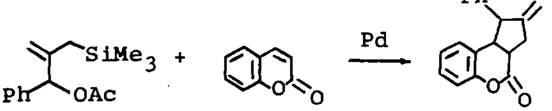
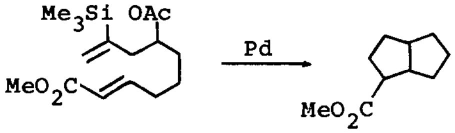


(191)

By selection of a suitable structure for the substituent, intramolecular $[3_\pi + 2_\pi]$ cycloaddition may be realized simultaneously affording two five-membered rings [72, 73].

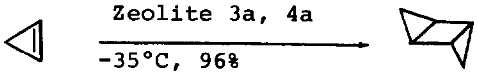


(192)

The wide synthetic potential of Trost's method has been used to obtain natural cyclopentanoids of complicated structure. A recent review [74] summarizes the relevant data. At the same time, Binger's and Trost's methods have the principle disadvantage of poor availability of the starting compounds. To obtain them one must use stoichiometric amounts of organometallic reagents (sodium or potassium amide, butyllithium, lithium diisopropylamide) [74, 75]. This disadvantage is a serious obstacle to broad application of these methods.

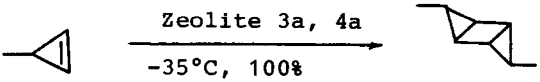
5. HOMO-CYCLOADDITION OF CYCLOPROPENES

As cyclopropene is labile it could be cyclooligomerized only at low temperatures (-35°c) using zeolite catalysts [76, 77]. Gaseous cyclopropene diluted with argon after passing through columns packed with zeolite 3a or 4a is converted into trans-tricyclo[3.1.0.$0^{2,4}$]hexane [193) in 96%yield.



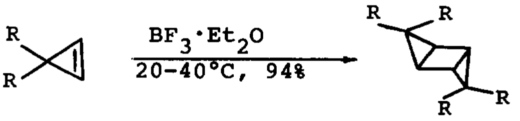
(193)

Under the same conditions 3-methycyclopropene quantitatively forms the $[2_\pi + 2_\pi]$ dimer (194) [76, 77].



(194)

With zeolite 5a the yields of dimers (193, 194) fall to 69% [73, 74]. Lewis acids [$BF_3 \cdot Et_2O$, $Et_2O \cdot AlCl_3$, $AlEt_3 \cdot Et_2O$, and BEt_3] also catalyze the $[2\pi + 2\pi]$ cyclodimerization of cyclopropenes [78, 79].



R = CH_3 (195) 94%

(196)

Cyclopropene homodimerization can be realized in the presence of homogeneous metal complex catalysts. Thus, 1-methylcyclopropene which is converted into higher oligomers under the influence of zeolite catalysts or on heating, in the presence of $PdCl_2$ at 20°C is quantitatively dimerized into a mixture of isomeric 1,2- and 1,4-dimethyltricyclo[3.1.0.0^{2,4}]hexanes [80, 81].

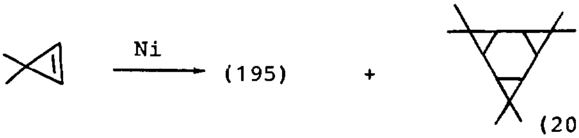
(197) 2:1 (198)

This strongly exothermic reaction should be carried out in diluted solutions in toluene, pentane, THF, ether, ethanol, or methylene chloride [80]. 1-Methylcyclopropene cyclodimerization is catalyzed also by $PdBr_2$, PdI_2, $Pd(NO_3)_2$, $(\pi\text{-}C_3H_5PdCl)_2$, and $(PhCN)_2Pd$, $PdCl_2$ [80, 81].

1,3,3-Trimethylcyclopropene is less active in the cyclodimerization and on treatment with $(\pi\text{-}C_3H_5PdCl)_2$ complex gives the corresponding hexamethyltricyclohexanes in only 10% yield [80, 81].

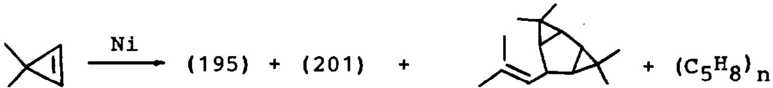
(199) 1:1 (200) 90%

The most thorough investigation into the regularities of catalytic cycloologomerization has been undertaken for 3,3-dimethylcyclopropene (3,3-DMCP) which is the most stable of all cyclopropenes known [82, 87]. When zero-valent Ni complexes activated by organophosphorus ligands are used $[2_\pi + 2_\pi]$ cyclodimerization into trans-3,3,6,6-tetramethyltricyclo[3.1.0.0^{2,4}]-hexane (195) is the major reaction and the cyclctrimer (201) is formed in minor quantity [82].



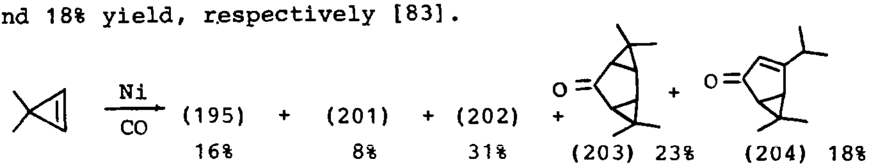
(201)

3.3-Dimethylcyclopropene under the action of a catalytic amount of $Ni(CO)_4$ undergoes non-selective transformations giving the trimer (202) as well as the dimer (195) and trimer (201); more than a third of the total amount of the monomer is converted into higher oligomers [82, 83].

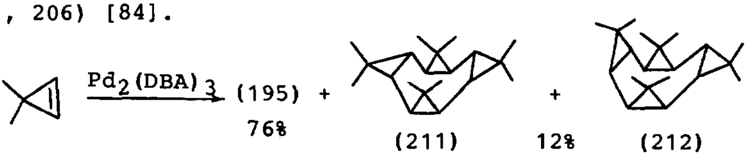


44% 14% (202) 36%

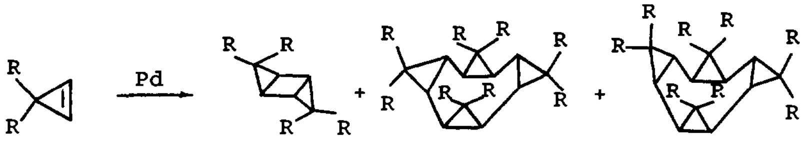
If this reaction is carried out under gaseous CO (1 atm.) the formation of the higher oligomer is completely prevented [83] and the cyclic ketones (203) and (204) are formed in 23 and 18% yield, respectively [83].



Increase in the CO pressure to 60-70 atm. raises the selectivity for ketone (203) to 54% [83]. In the presence of Pd complexes [Pd(DBA)$_2$, Pd(COD)$_2$, or catalyst prepared in situ by AlEt$_2$(OEt) reduction of Pd(acac)$_2$], 3,3-dimethylcyclopropene is converted into a mixture of dimer (195) and the two tetramers (205, 206) [84].

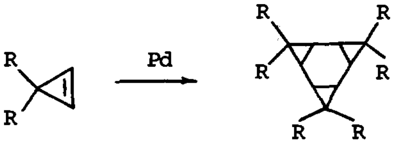


3-Methyl-3-ethyl- and 3,3-diethyl-cyclopropenes, and spiro-[4.2]hept-1-ene react in a similar way [85].



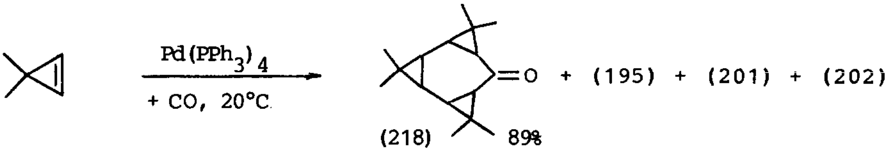
R = CH$_3$ R = C$_2$H$_5$	(207) 82%	(208)	14%	(209)
R = R = C$_2$H$_5$	(210) 71%	(211)	16%	(212)
R = R -(CH$_2$)$_4$-	(213) 53%	-	15%	(214)

On introduction of organophosphorus activators into Pd-containing catalysts, the cyclopropene cyclooligomerization shifts towards the predominant formation of trimeric σ-trishomobenzene (201). The reaction selectivity by the trimer can reach ca.~100% depending on the nature of the organophosphorus ligand and the Pd:PR$_3$ molar ratio [82-84].



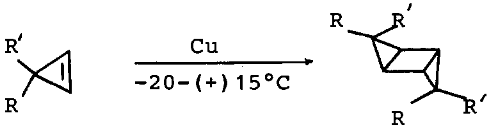
R = R = CH$_3$	(201)	97%
C$_2$H$_5$	(215)	99%
R = CH$_3$ R = C$_2$H$_5$	(216)	95%
R = R = -(CH$_2$)$_4$-	(217)	

The highest selectivity of Pd-catalyst for trimers (201, 215-217) is observed when electron-accepting organophosphorus ligands are used [PR_3, $P(OR)_3$, tris(o-phenylphenyl)-phosphite] at a Pd:PR_3 molar ratio of 1:4 [82-84]. Increase in the solvent polarity (benzene, diethyl ether, acetone) reduce the yield of σ-trishomobenzene from 100 to 74% while the [$2_\pi + 2_\pi$] dimer proportion grows up to 25% [84]. If the 3,3-dimethylcyclopropene reaction is carried out under CO [$Pd(PR_3)_4$ catalyst], the seven-membered ketone (218) becomes the main product [86].



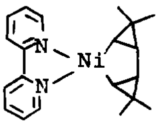
(218)

3,3-Dimethyl-, 3-methyl-3-cyclopropyl cyclopropene and spiro[2.3]hexene-1 dimers (219) are formed by homo [$2_\pi + 2_\pi$] cycloaddition in quantitative yield in the presence of monovalent copper complexes $(PhO)_3P{\cdot}CuCl$ and $Ph_3P{\cdot}CuCl$ [87].



R = R' = CH_3 (195)
R = CH_3 R' = ▷ (220)
R = R' = $-(CH_2)_3-$ (221)

Monomer (219) is rather interesting due to its ability to enter [$2_\pi + 2_\pi$] cyclodimerization in 100% yield not only when catalyzed, but also in 10 min at 60-80°C [87]. Papers [88-94] contain important data on the mechanism of cyclooligomerization of 3,3-dimethylcyclopropene under the influence of Ni, Pd, and Rh complexes. Binger and his coworkers have been able to isolate a series of intermediatory metallocycles (222-227) the structures of which have been established by spectral methods, chemical transformations, and X-ray analysis



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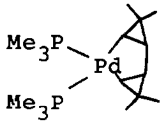

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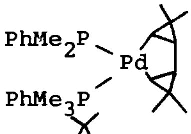

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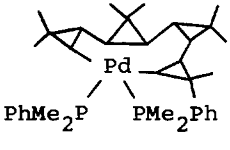

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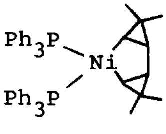

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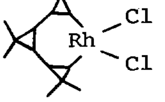
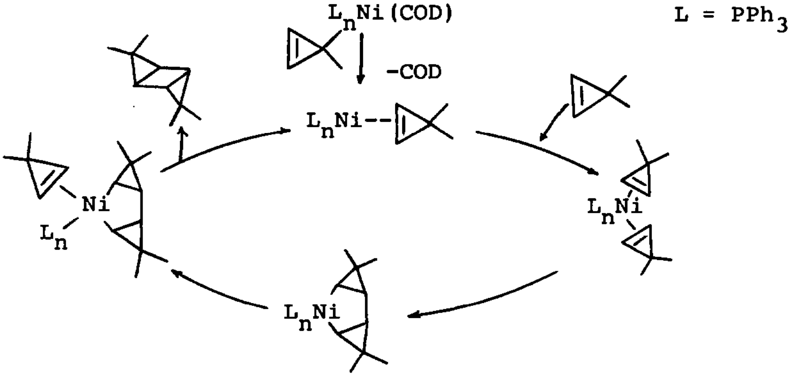


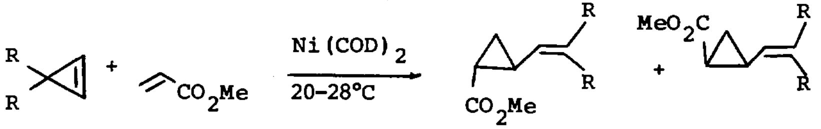
(227)

Complexes (222-227) generate the 3,3-DMCP dimer (195) and tetramer (205) on heating or treatment with maleic anhydride. That is why the complexes are regarded as playing the key role in the reaction mechanisms. For example, the mechanism for the dimerization in the presence of the $Ni(COD)_2$-PPh_3 catalyst may be represented as follows:



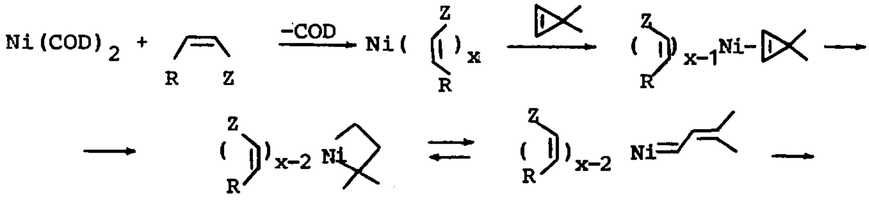
5.1. Cross-Cycloaddition of Cyclopropenes to Linear Olefins

An unusual reaction of [2+1] cycloaddition of 3,3-disubstituted cyclopropenes to olefins catalyzed by Ni complexes was discovered in 1974 [82, 95].

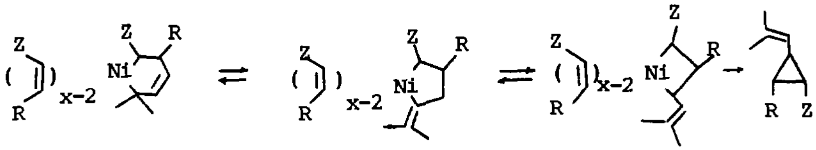


$R = R = CH_3$	39%	(228)	1:1	(229)
Ph	85%	(230)	9:1	(231)
$R = CH_3$ $R = Ph$	51%	(232)	2:1	(233)

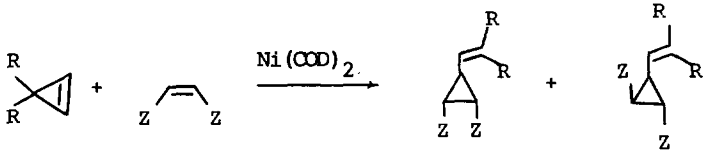
The structures of the codimers (228-233) suggest the opening of the unsaturated three-membered ring followed by the formation of a new saturated one. The mechanism proposed by the authors for this transformation involves a key step for the rupture of C_1-C_3 bond in the three-membered ring and the formation of Ni-cyclobutane or Ni-carbene complexes (234, 235):



(234) (235)



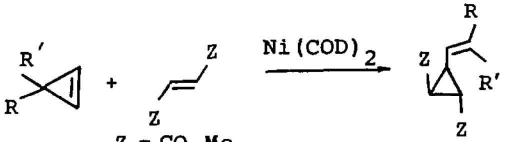
In the presence of Ni(COD)$_2$, 3,3-dimethyl- and 3,3-diphenyl cyclopropenes stereospecifically react with dimethyl maleate affording 3-alkenyl substituted cis-1,2-cyclopropanedicarboxylic acid methyl eaters in 60-65% yield [95]. Under the reaction conditions dimethyl maleate undergoes partial isomerization into dimethyl fumarate which in turn enters the [2+1] cycloaddition forming the trans-cyclopropanedicarboxylic acid diester (237).



$Z = CO_2CH_3$ $R = CH_3$ 60%   (236) 97:3   (237)

Ph   65%   (238) 79:21   (239)

Under the same conditions, individual dialkyl fumarates usually form only trans-cyclopropanedicarboxylic acid diesters in a higher yield (up to 87%) [95].



$Z = CO_2Me$

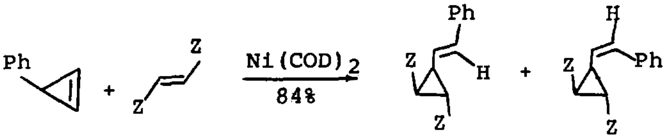
$R = R' = CH_3$ (237)

$R = Ph$ $R' = CH_3$ (239)

$R = CH_3$ $R' = C_2H_5$ (240)

$R = Ph$, $R' = C_2H_5$ (241)

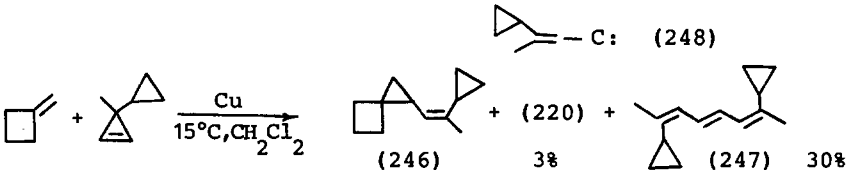
Similarly, 3-methyl-3-phenylcyclopropene adds to dialkyl fumarates to give two isomers of Z- and E-configuration in 1:9 ratio [95].



$Z = CO_2R$ $R = CH_3$ (242) 1:9   (243)

C_2H_5 (244)   (245)

The above examples show that Ni complexes catalyze cyclopropene [2+1] cycloaddition to activated olefins only. Nefedov and his coworkers have succeeded to involve other types of olefins in this reaction by using copper-containing catalysts [87, 96, 97]. It has been found that in the presence of the Cu complex $(PhO)_3P{\cdot}CuCl$, 3,3-disubstituted cyclopropenes interact with gem-disubstituted olefins giving [2 + 1] codimers (246, 249, 250) as the main products.



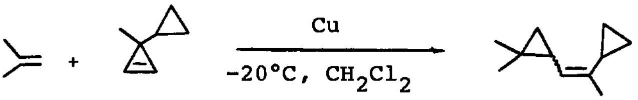
(248)

(246)

3%

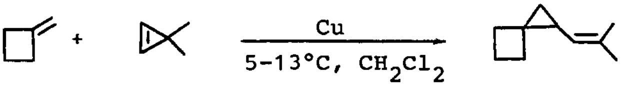
(247) 30%

A substantial amount of the 3-methyl-3-cyclopropylcyclopropene dimer (247) is formed, which established the vinylcarbene (248) as an intermediate. The [2 + 1] cycloaddition of 3-methyl-3-cyclopropylcyclopropene to isobutylene is also catalyzed by a copper complex.



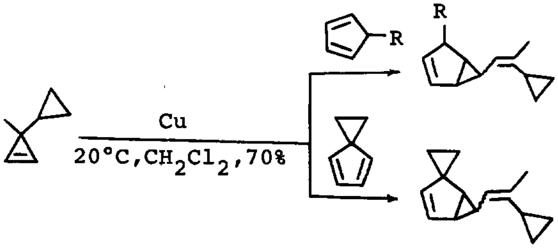
(249) 58%

3,3-Dimethylcyclo$\overset{o\,r}{rp}$opene enters a similar reaction with gem-disubstituted simple olefins [96].



(250) 30%

Monovalent copper complexes catalyze the [2 + 1] cycloaddition of cyclopropenes to cyclopentadiene-1,3 and its derivatives [96, 97].



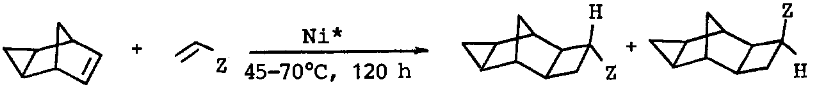
R = H (251)
Z/E = 2/1
R = CH_3 (252)
Z/E = 2/1
(253) Z/E = 2/1

The Cu-catalyzed cycloaddition of cyclopropenes to mono- and 1,2-di-substituted olefins according to the [2 + 1] scheme proceeds with difficulty and gives low yields (butene-1 - 8%, cyclooctene - 10%), and cyclopropene isomerization into vinylcarbene followed by dimerization into the corresponding triene become the principal reaction.

6. SYNTHESIS OF CYCLOBUTANES VIA CYCLOADDITION OF NORBORNENES OR NORBORNADIENES

6.1. Reactions of Norbornenes and Norbornadienes with Linear Olefins

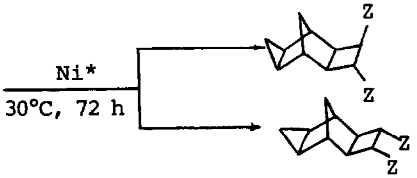
All attempts to carry out [2π + 2π] cycloaddition of the simplest alkenes to norbornene using homogeneous metal complex catalysts have been fruitless. Some examples of such interaction are known only for exo-tricyclo[3.2.1.0^{2,4}]octene-6 (254) which carries an annelated cyclopropane moiety to provide additional activation of the double bond [98].



(254) Z = CN 55% (255) (256)

CO_2Me 72% (257) (258)

(254)

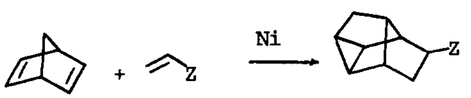


(259) 72%

(260) 30%

Ni* = $Ni(CH_2{=}CH{-}CN)_2$

Norbornadiene is very reactive in cyclodimerization with olefins bearing electron accepting substituents. The extremely selective process to give [4π+ 2π] codimers is catalyzed by Ni complexes such as $Ni(CO)_4$, $Ni(CO)_3(PPh_3)$, $Ni(CO)_2[P(OPh)_3]_2$, $Ni[P(OPh)_3]_4$, $Ni[P(OEt)_3]_4$, $Ni(COD)_2$, $Ni(CH_2{=}CH{-}CN)_2$, $Ni(CN)_2(PPh_3)_2$, and by the $Ni(acac)_2{-}PPh_3{-}Et_2AlCl$ system [99-111]. [4π+ 2π] Cyclocodimerization can also be carried out under the influence of Co-containing catalysts, particularly $Co_2(CO)_8{-}2PPh_3$ [108]. The $Ni(CH_2{=}CH{-}CN)_2$ complex is the most active of the Ni- and Co-catalysts giving yields of codimers (261-263) of ca.~70-95%.

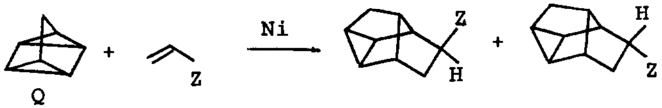


Z = CN (261) 95%

CO_2Me (262) 82%

COMe (263) 70%

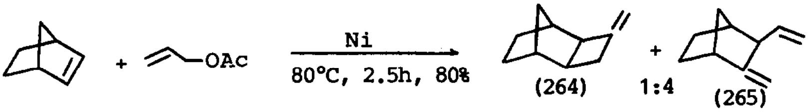
The reactivity of olefins bearing electron-acceptor substituents in the codimerization with NBD decreases in the following series: acrylonitrile, crotononitrile, methacrylonitrile, dimethyl maleate [108, 109]. Codimers (261-263) are formed as mixtures of exo- and endo-isomers. Their ratio is mainly determined by the organophosphorus ligand or solvent nature and does not depend on the size of the alkyl group of ester [109, 110]. In particular, bulky organophosphorus ligands as catalyst activators favour the formation of exo-isomers while increase in the solvent polarity (change of THF or ethyl acetate for methanol or acetonitrile) causes an almost ten-fold rise in the proportion of endoisomer [107]. The bis-acrylonitrile Ni complex catalyzes the activated olefin cycloaddition to the NBD valence isomer, quadricyclene [110]. Similar products are formed as in the case of NBD (261, 262) though in somewhat lower yield.



Z = CN 50% (261)a 1:1 (261)b

CO_2 Me 58% (262)a 3:2 (262)b

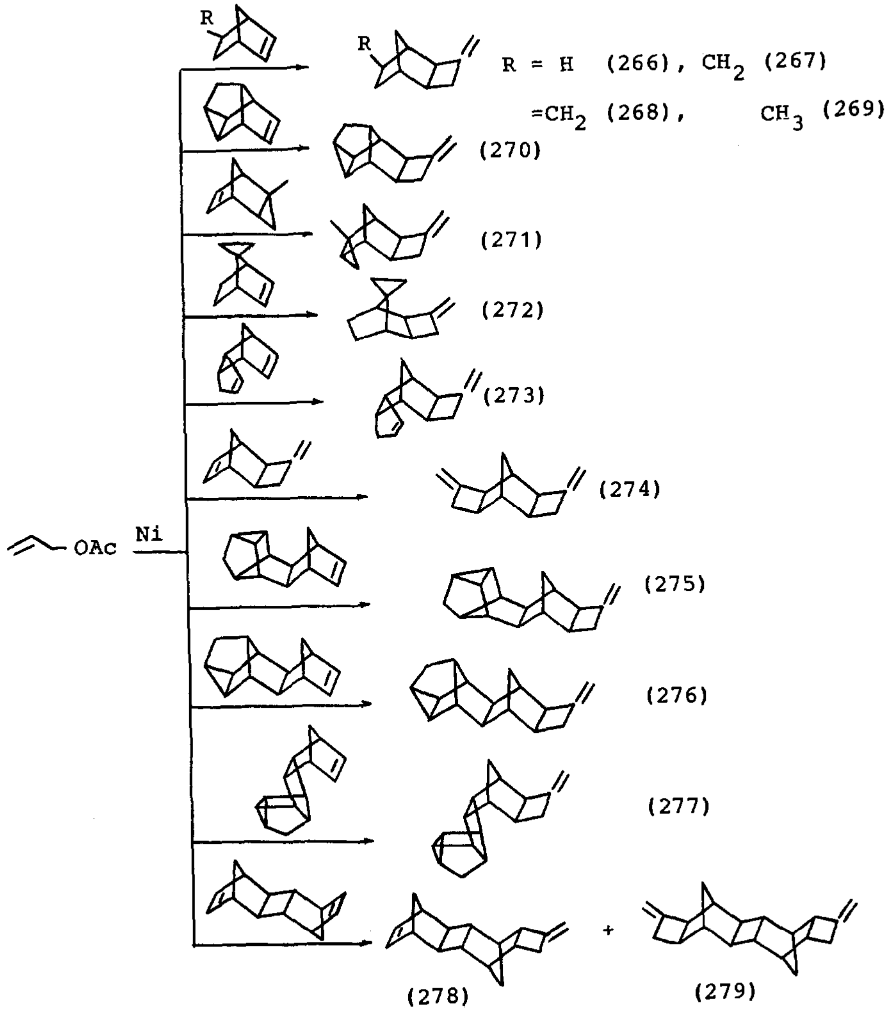
The codimerization of allylacetate and norbornene in THF in the presence of the Ni[P(i-PrO)$_3$]$_4$ complex [111] is significant.

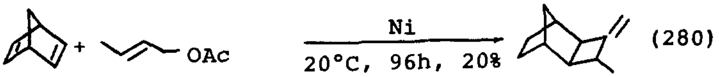


Acetic acid is eliminated in this reaction while in formation of the methylenecyclobutene isomer (264) allyl acetate acts not as an olefin but as an allene equivalent (hydrocarbon (264) formally represents an NB adduct to allene resulting from [2π+ 2π] cycloaddition).

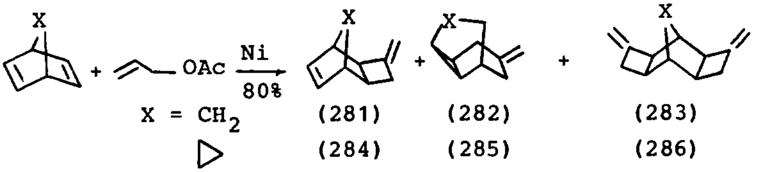
Later, authors of the present paper offered a highly selective and universal three-component catalyst for the [2π+ 2π] cycloaddition of the C_3H_4-moiety originating from allyl acetate to NB or its derivatives, Ni(acac)$_2$-P(OR)$_3$-AlEt$_3$ (R= i-Pr, sec-Bu, cyclohexyl) [112-114]. The efficacy of the catalyst has been proven in the synthesis of broad variety of polycyclic compounds containing the methylenecyclobutane moiety [112].

Crotyl acetate is another allyl ester able to enter the reaction with NB, though less readily [112].





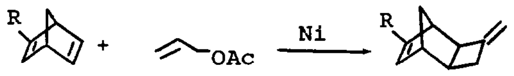
The three-component system $Ni(acac)_2$-$P(i\text{-}PrO)_3$-$AlEt_3$ catalyzes allyl acetate cycloaddition to norbornadiene or 7-SCNBD (SC - spirocyclopropane). The reaction here proceeds in a complicated way and gives three types of hydrocarbons (281-283) [115].



(281) (282) (283)

(284) (285) (286)

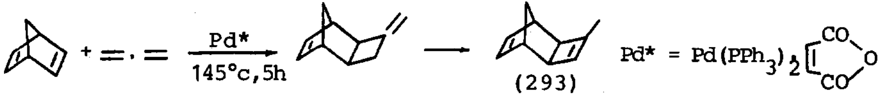
It is interesting to note that allyl acetate enters into cyclodimerization with NBDs bearing polyr substituents, by $[2\pi + 2\pi]$ cycloaddition at the double bond which does not carry an additional substituent [115].



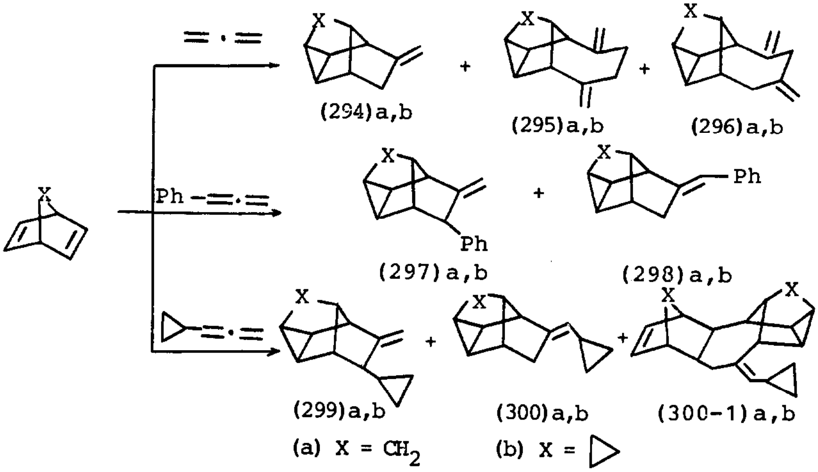
R = CH_2OH (287) 50%
CH_2OMe (288) 83%
CH_2OAc (289) 55%
CO_2Me (290) 96%
Cl (291) 76%

6.2. Cycloaddition of Norbornadienes to Allenes and Acetylenes

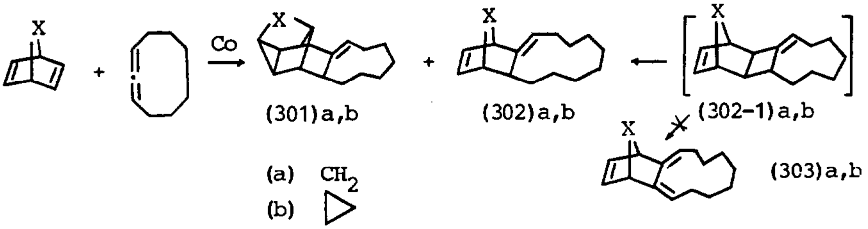
The scope of "σ-strained" monomers suitable for cycloaddition to 1,2-dienes is limited to NBD and its spirocyclopropane analogue (7-SCNBD) (292) [116-123]. Thus, under the influence of Pd° complexes, unsubstituted allene and NBD give the codimer (293) of an unusual structure which formally is the product of methylacetylene $(2\pi + 2\pi]$ cycloaddition to bicyclo[2.2.1]hepta-2,5-diene [116, 117]. However, attempts to carry out a direct reaction between NBD and methylacetylene under the same conditions have failed. The isomerization of the unsaturated bond may occur after the allene $[2\pi + 2\pi]$ cycloaddition to NBD. The reaction may be represented as a multi-step process involving an obligatory step of methylene double bond isomerization according to the following scheme:



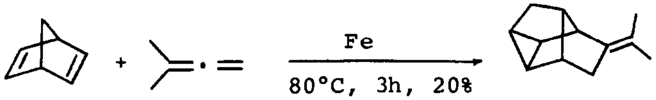
Contrary to Pd° complexes, catalysts based on Co or Fe compounds accomplish mainly $[4\pi + 2\pi]$ cycloaddition of 1,2-dienes to NBD or 7-SCNBD, furnishing polycyclic hydrocarbons of "deltacyclene" structure [118-123]. Thus, on cooligomerization of NBD or (292) and allene, cyclopropylallene, phenylallene, or 1,2-cyclononadiene in the presence of Co(acac)$_2$-diphos-AlEt$_2$Cl catalyst, $[4\pi + 2\pi]$ cycloaddition becomes predominant [isomers (294a, b; 297a,b; 299a,b)]. The nature of the substituent in the allene markedly influences the direction of the reaction and favours the original cycloaddition types, resulting in structures like (295a,b; 296a,b; 302 a,b).



The reaction of NBD or (292) and a cyclic allene, 1,2-cyclononadiene is unusual. Apart from the expected $[4\pi + 2\pi]$ cyclodimerization, $[2\pi + 2\pi]$ cycloaddition of 1,2-cyclononadiene to NBD [or (292)] may take place leading to intermediate (302-1)a,b , which undergoes an unexpected rearrangement into the final product (302)a,b possessing the 1,4-diene double bond system instead of the expected 1,3-diene (303)a,b [120, 123].

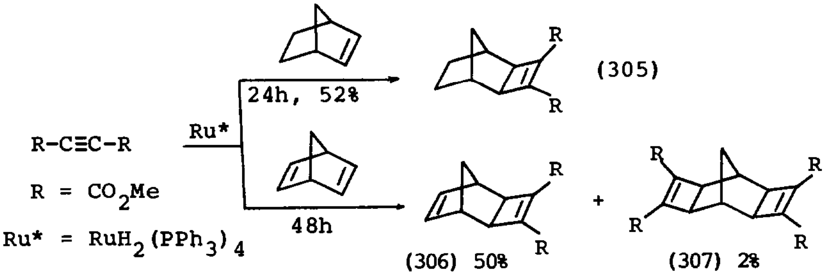


1,2-Diene cycloaddition to NBD has been studied in the presence of iron-containing catalysts in the case of 1,1-dimethylallene [118, 119]. The latter undergoes [4π+ 2π] cyclization with NBD under the action of Fe(acac)$_3$-Ph$_2$P(CH$_2$)$_2$PPh$_2$-AlEt$_2$Cl catalyst and affords 8-isopropylidenedeltacyclene in 20% yield [118, 119].

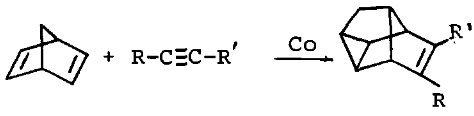


(304)

The cycloaddition of acetylene monomer to NB and NBD, catalyzed by Ni, Co, or Ru complexes is one of the important methods for preparing strained polycyclic compounds. The type of the reaction in the cycloaddition of acetylene to NB or NBD is mainly determined by the nature of the metal and of the substituent in the acetylene [124]. For example, Ru complexes favour selective [2π + 2π] cyclocodimerization [124].

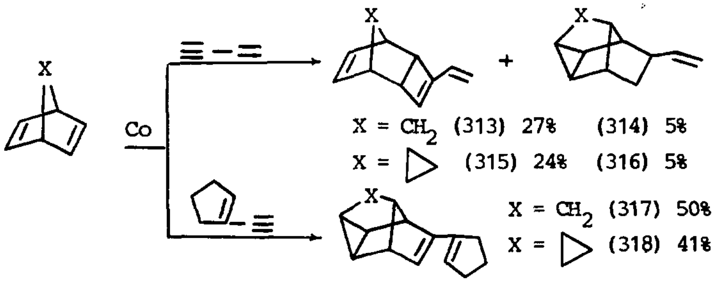


The RuH$_2$(CO)[P(p-PhF)$_3$]$_3$ catalyst gives a high yield (ca.~88%) of the cyclooligomers [125]. A similar reaction is undergone by the NBD valence isomer quadricyclane [126]. Unlike Ru complexes, low valency Co ones obtained by diethylaluminium chloride reduction of Co(acac)$_3$ direct the interaction between NBD and acetylenes in the presence of 1,2-bis(diphenylphosphino)ethane exclusively towards $[4\pi + 2\pi]$ codimers [127-130].



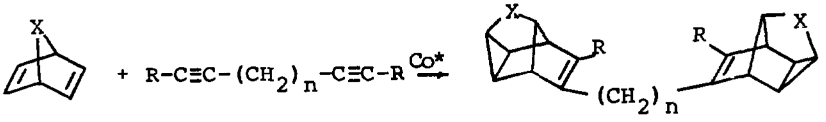
R = R' = H (308) 44%
R = H, R' = Ph (309) 17%
R = H, R' = CH_3 (310) 14%
R = H, R' = C_2H_5 (311) 12.5%
R = R' = Ph (312) 24%

The three-component Co(acac)$_2$-PPh$_3$-AlEt$_2$Cl system at a Co:P:Al ratio of 1:2:10 is the most selective catalyst for the cycloaddition of acetylenes to NBD [123, 131]. The selectivity of this catalyst for cyclocodimers attains ca.~95%, when there is an excess of PPh$_3$ (Co:P = 1:2) and on increased concentration of starting acetylene (acetylene:NBD = 1.2:1). The acetylene here acts as a ligand-activator. This system effectively catalyzes cycloaddition of vinylacetylenes (VA) to NBD and (292) when the direction of the reaction is strongly dependent on the former's structure [131]. Thus, the cycloaddition of vinylacetylene to NBD predominantly follows the $[2\pi + 2\pi]$ scheme via the unusual endo-attack on the NBD double bond [isomer (313)]. Unlike VA, 1-ethynyl-1-cyclopentene reacts with NBD or (292) with the above catalyst by the "usual" $[4\pi + 2\pi]$ cycloaddition scheme [123, 131].



X = CH_2 (313) 27% (314) 5%
X = ▷ (315) 24% (316) 5%
X = CH_2 (317) 50%
X = ▷ (318) 41%

Diacetylenes also very actively undergo $[4\pi + 2\pi]$ cyclooligomerization with NBD and 7-SCNBD with Co catalysts [123, 131]. This is a valuable reaction providing a good and simple route to bis-deltacyclenes (319a,b - 322a,b) which otherwise are poorly available.

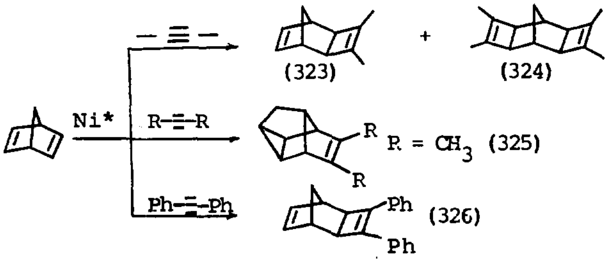


(a) X = CH_2 R = H n = 2 (319)a,b; n = 3 (320)a,b; n = 4 (321)a,

(b) ▷ R = Ph n = 0 (322)a,b

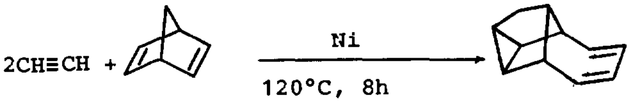
Co* = $Co(acac)_2$-PPh_3-$AlEt_2Cl$

Ni Catalysts make it possible to carry out the cycloaddition of acetylenes to NBD by the known [2_π + 2_π] and [4_π + 2_π] schemes [108, 132].



Ni* = $Ni(CO)_2(PPh_3)_2$,
$Ni[P(OC_8H_{17})_3]_4$

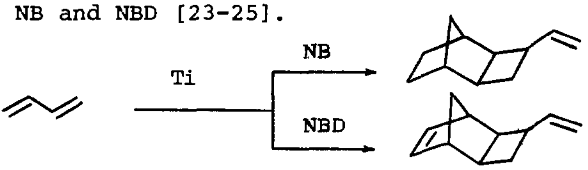
In the case of ethyne, the reaction involving two molecules of acetylenes catalyzed by $Ni(CO)_2(PPh_3)_2$ proceeds according to the [4_π + 2_π + 2_π] cycloaddition scheme [108].



(327) 5%

6.3. Cycloaddition of NBs and NBDs to 1,3-Dienes

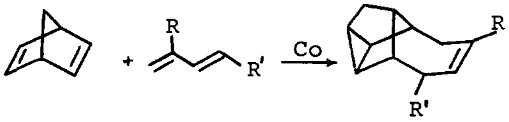
Cyclooligomerization of NB, NBD, and dicyclopentadiene with 1,3-dienes, catalyzed by Ti, Fe, Co, and Ni complexes has been studied in most detail. The 1,3-diene cycloaddition to the above "σ-strained" monomers may follow one of three schemes, [4_π + 2_π], [2_π + 2_π], or [4_π + 4_π], depending on the metal type. Thus, Ti complexes favour selective $[2_\pi + 2_\pi]$ cycloaddition of butadiene both to NB and NBD [23-25].



(328) 90%

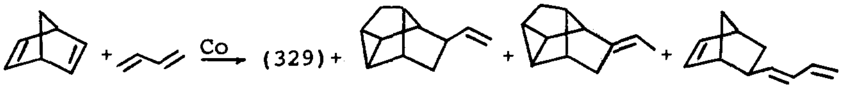
(329) 90%

With the Co(acac)$_3$-diphos-AlEt$_2$Cl or CoCl$_2$-diphos-AlEt$_2$Cl catalysts, the $[4_\pi + 4_\pi]$ cycloaddition to NBD is undergone by butadiene, isoprene, and piperylene [133-136].



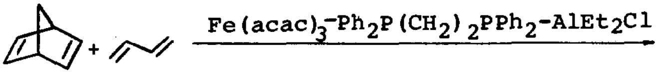
R = R' = H (330)
R = CH$_3$ R' = H (331)
R = H R' = CH$_3$ (332)

On change of AlEt$_2$Cl in the three-component catalyst for AlEt$_3$, butadiene and NBD react according to $[2_\pi + 2_\pi]$ and $[4_\pi + 2_\pi]$ cycloaddition schemes giving respectively codimers (329) and (333). Under the reaction conditions, the latter undergoes partial isomerization into the thermodynamically more stable compound (334) [137]. The codimer yields were not reported in [137] though 2-butadienylnorbornene (335) was reported to be the major reaction product, and not isomers (329, 333, 334).



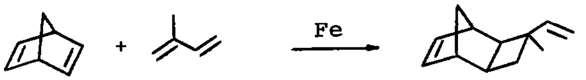
(333) (334) (335)

The reaction of NBD and butadiene upon Fe-, Ni-, and Mn-based catalysts has been investigated in [118, 133]. Fe Complexes are the most effective, catalyzing the $[2_\pi + 2_\pi]$ and $[4_\pi + 2_\pi]$ cycloaddition of NBD to butadiene.



(329) + (330)

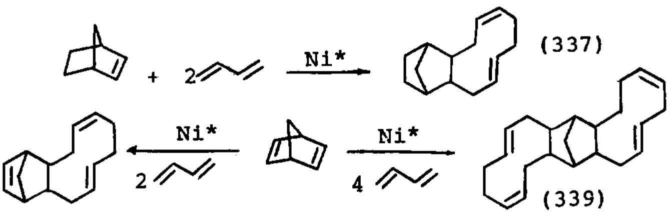
Under similar conditions, isoprene and NBD show exclusively the $[2_\pi + 2_\pi]$ interaction [138].



(336)

Ni and Mn Complexes turn out to be poorly active. Thus, in the presence of Mn compounds $[2_\pi + 2_\pi]$ codimer (329) yield does not exceed 8% [118].

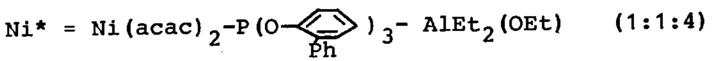
Zero-valent Ni complexes direct butadiene cooligomerization with NB and NBD towards cyclododeca-1,5-diene (337-339) derivatives, and no formation of a novel strained ring is observed [139].



(337)

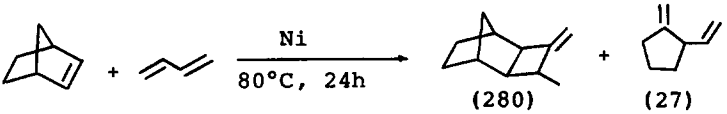
(338)

(339)



$Ni^* = Ni(acac)_2\text{-}P(O\text{-}C_6H_4Ph)_3\text{-}AlEt_2(OEt)$ (1:1:4)

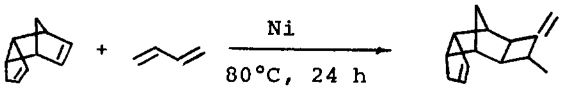
Ni Hydride complexes are a special class of Ni-containing catalysts and bring about the $[2_\pi + 2_\pi]$ cycloaddition of butadiene to norbornene and to dicyclopentadiene [140-143]. The most active catalyst is prepared by $NaBH_4$ reduction of the $(n\text{-}Bu_3P)_2NiBr_2$ complex [141]. The selectivity of butadiene cycloaddition to NBD is determined by the $(n\text{-}Bu_3P)_2NiBr_2$:$NaBH_4$ molar ratio.



(280) 60%

(27) 12%

A satisfactory yield (60%) of codimer (280) has been obtained with an equimolar ratio of the catalyst components. Another obligatory condition is the use of alcoholic media, ethanol being the best solvent [140-143]. Butadiene homodimer (27) is formed in minor amount together with (280). In the case of endo-dicyclopentadiene, the yield of $[2_\pi + 2_\pi]$ codimer (340) is 73% [142, 143].

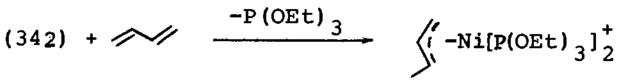


(340) 73%

A similar reaction is brought about by $Ni[P(OEt)_3]_4$ which is active only in the presence of Brensteadt acid (CF_3COOH) [141, 143]. The results obtained for (341) are important for understanding the reaction mechanism. It is known that the interaction of (341) and an acid is characterized by the following equilibrium:

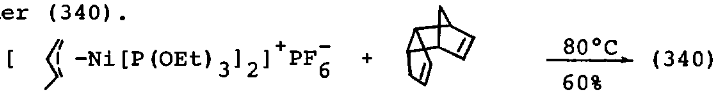
$$\underset{(341)}{HX + Ni[P(OEt)_3]_4} \longrightarrow \underset{(342)}{\left\{HNi[P(OEt)_3]_4\right\}^+X^-}$$

Ni Hydride (342) gives the π-crotyl complex (343) with 1,3-dienes [144].



(343)

The authors of refs [140-143] ascribe the key role to complex (343) in forming butadiene codimers with Nb and endo-cyclopentadiene. This conclusion is reliably supported by the results of experiments with an authentic stable π-crotyl complex, syn- -crotyl bis(triethoxyphosphine)nickel hexafluorophosphate (344) [142, 143]. This complex reacts quite smoothly with endo-dicyclopentadiene in ethanol at 80°C to give a 60% yield of $[2_{\pi} + 2_{\pi}]$ codimer (340).



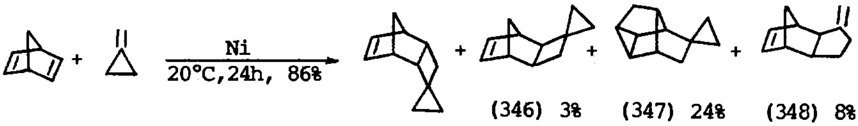
(344)

In the absence of the acid, complex (344) catalyzes the codimerization of DCPD and butadiene into (340).

The stereochemistry of the codimers obtained (280, 340) should be determined at the step of the insertion of the strained olefin (NB or DCPD) into the $Ni-\eta 3-C_4H_7$ bond. It has been shown in [145] that this reaction is the exo-cis-carbometallation of the unsaturated bond. This results in the exo-configuration of the polycyclic compounds formed (280, 340) [140-143].

7. CROSS-REACTION OF "σ-STRAINED MONOMERS

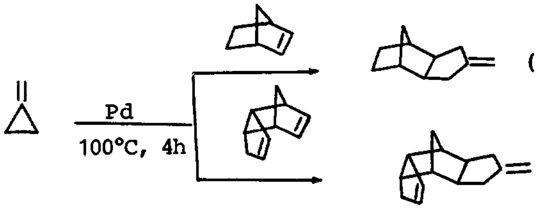
The cross-cycloaddition reactions of mutually σ-strained monomers occupy an important position among other methods for preparing strained and polycyclic compounds which are not otherwise readily available. The reaction between methylenecyclopropane and NBD in the presence of PPh_3-activated $Ni(COD)_2$ [146] was one of the first examples. The cycloaddition follows three different paths, those to the [$2\pi + 2\pi$] [isomers (345, 346)] and [$2\pi + 2\pi + 2\pi$] [isomer (347)] being predominant. The amount of [$3\pi + 2\pi$] codimer (348) is low. The total absence of NBD and MCP homodimers is interesting.



(345) 50%   (346) 3%   (347) 24%   (348) 8%

With Pd-based catalysts, [$3\pi + 2\pi$] cycloaddition becomes the only reaction [147-149]. The $Pd(DBA)_2$-$(i\text{-}Pr)_3P$ (1:1) system shows high activity and catalyzes the codimerization of methylcyclopropane and NBD or endo-DCPD [147-149].

The yields of tri- and tetracyclic codimers are rather high (78 and 74%). Hydrocarbons (349, 350) have also been obtained in the same yield with the $Pd(acac)_2$-$P(i\text{-}Pr)_3$-$AlEt_2(OEt)$ (1:1:2) catalyst.



(349)

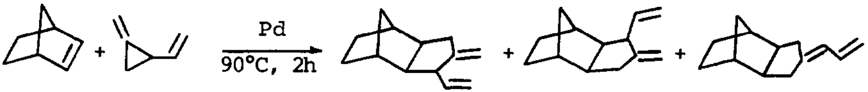
(350)

The reaction shows high stereo- and regio-selectivity for the exo-side of the NB double bond. NBD, Possessing two identical double bonds, adds two MCP molecules under the same conditions [148, 149].

(351) (352)

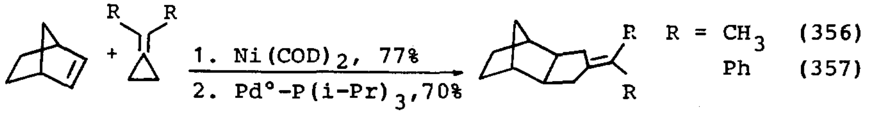
The yield and isomer composition of codimers (351, 352) depend on the molar ratio of the monomers. With MCP in excess (NBD:MCP = 1:2), both isomers are formed in 46% yield. With the NBD:MCP = 2:1, only isomer (351) is formed in 80% yield.

NB Undergoes cyclocodimerization with 1-methylene-2-vinyl-, 1-isopropylidene-, 1-diphenylidene-, and 2-phenyl-1-phenylidenecyclopropanes [53, 150, 151]. The first forms a mixture of three codimers (353-355) in a total yield of 71% under the influence of $Pd(DBA)_2$-$P(i\text{-}Pr)_3$ [53].



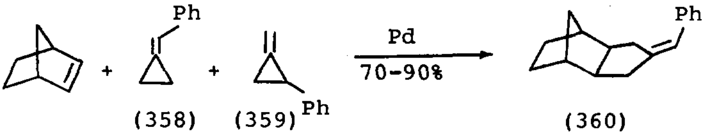
(353) (354) (355)

The codimerization of NB with 1-isopropylidene- and 1-diphenylidene cyclopropanes is catalyzed both by Ni° and Pd° complexes, by $[3_\pi + 2_\pi]$ cycloaddition [150].



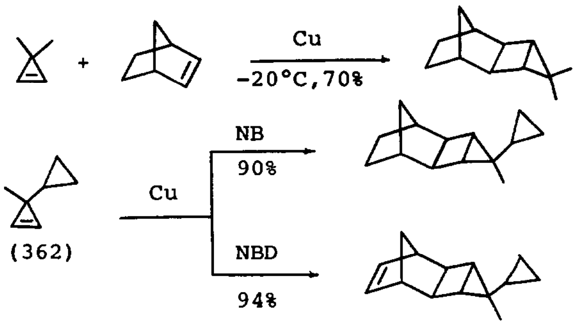
(356)
(357)

The identical codimer (360) has been obtained on the ineraction between isomeric monophenyl-substituted MCPs (358, 359) and NB catalyzed by $Pd_2(DBA)_3$-$P(i\text{-}Pr)_3$, 1:1 [151].



(358) (359) (360)

Copper (I) complexes have been found to assist [2 + 1] cycloaddition of cyclopropenes to NB olefins [96, 152]. Cu(I) Complexes with triphenylphosphine or triphenylphosphite are used as $[2_\pi + 2_\pi]$ cycloaddition catalysts. The selectivity for $[2_\pi + 2_\pi]$ cycloaddition depends on temperature and reaches 90-95% at -20°C.



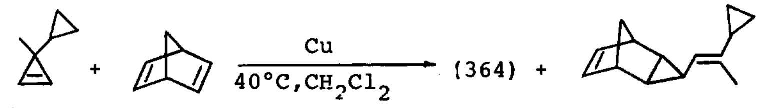
(361)

(362)

(363)

(364)

At elevated temperature, the reaction selectivity drops because of partial switching of the reaction to [2 + 1] cycloaddition.

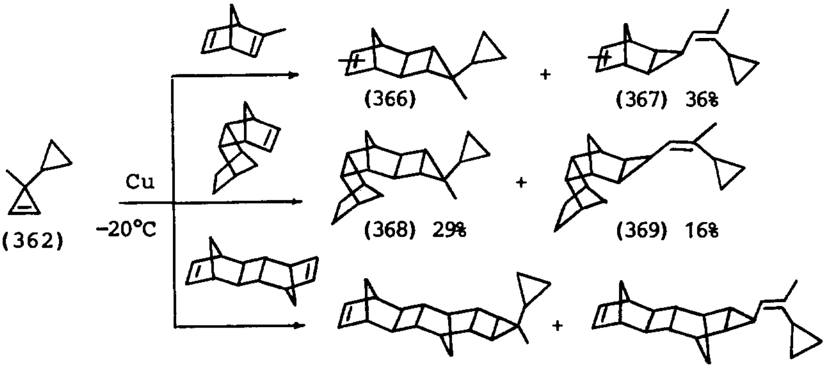


(362)

42%

(365)

The interaction between NB or NBD derivatives and 3-methyl-3-cyclopropylcyclopropene (362) under optimal conditions (CH_2Cl_2, -20°C) proceeds non-selectively by both $[2_{\pi} + 2_{\pi}]$ and [2 + 1] cycloaddition modes [96, 152].



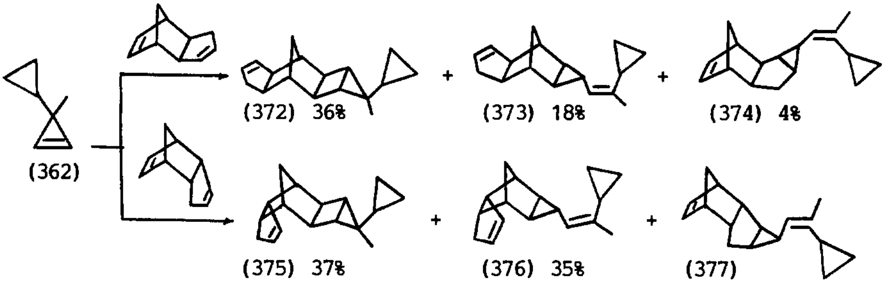
(362)

(366) + (367) 36%

(368) 29% + (369) 16%

(370) 11% + (371) 9%

Exo- and endo-dicyclopentadienes similarly react with 3-methyl-3-cyclopropylcyclopropene [96].



(362)

(372) 36%

(373) 18%

(374) 4%

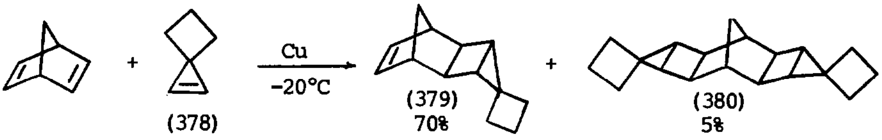
(375) 37%

(376) 35%

(377)

As is seen from the structure of the isomers obtained [267, 270), both norbornene and cyclopentene types of double bonds in DCPD enter into [2 + 1] cycloaddition [96].

Unlike 3,3-dimethyl- and 3-methyl-3-cyclopropylcyclopropenes, spiro[2.3]hexene-1 (378) adds to NBD in the presence of $(PhO)_3P{\cdot}CuCl$ at -20°C exclusively via $[2\pi + 2\pi]$ cycloaddition [96].



(378)

(379) 70%

(380) 5%

REFERENCES

1. U.M.Dzhemilev, R.I.Khusnutdinov, G.A.Tolstikov, Uspekhi Khimii, 57 (1987) 65.
2. P.Heimbach, W.Brenner, Angew. Chem., 79 (1967) 813.
3. W.Brenner, P.Heimbach, H.Hey, E.W.Müller, G.Wilke, J.Liebigs Ann.Chem., 727 (1969) 161.
4. E.G.Chepaikin, M.L.Khidekel, Izv.Acad.Nauk SSSR, Ser.Khim., (1971) 1129.
5. E.G.Chepaikin, M.L.Khidekel, U.S.S.R. 521,923; C.A. 85 (1976) 13127v.
6. W.Wiese, Dissertation, Ruhr-Universität, Bochum, 1972.

7. W.E.Billups, I.H.Cross, C.V.Smith, J.Am.Chem.Soc., 95 (1973) 3438.
8. P.Heimbach, H.Hey, Angew.Chem., 82 (1970) 550.
9. P.Heimbach, Angew.Chem., 85 (1973) 1035.
10. B.Bussemeier, Dissertation, Ruhr-Universität, Bochum, 1973.
11. H.I.Hey, Dissertation, Ruhr-Universität, Bochum, 1973.
12. C.R.Graham, L.M.Stephenson, J.Am.Chem.Soc., 99 (1977) 7098.
13. J.Kiji, K.Masui, J.Furukawa, Tetrahedron Lett., 11 (1970) 2561.
14. J.Kiji, K.Masui, J.Furukawa, Bull.Chem.Soc. Japan, 44 (1971) 1956.
15. J.Kiji, K.Yamamoto, Sh.Mitani, S.Yoshikawa, J.Furukawa, Bull. Chem.Soc. Japan, 46 (1973) 1791.
16. J.Furukawa, J.Kiji, K.Masui, Jpn Kokai 74,466,308; C.A. 82 (1974) 3858v.
17. R.Grigg, T.R.B.Mitchell, A.Ramasubbu, J.Chem.Soc., Chem.Commun., (1979) 669.
18. R.Grigg, T.R.B.Mitchell, A.Ramasubbu, J.Chem.Soc., Chem.Commun., (1980) 27.
19. A.Bright, J.F.Malone, J.H.Nicholson, J.Powell, B.L.Shaw, J.Chem. Soc., Chem.Commun., (1971) 712.
20. E.Schmitz, R.Urban, U.Heuck, G.Zimmerman, E.Grundemann, J.Prakt. Chem., 318 (1976) 185.
21. E.Schmitz, U.Heuck, D.Habisch, J.Prakt.Chem., 318 (1976) 471.
22. A.Behr, W.Keim, Angew.Chem., 97 (1985) 326.
23. L.G.Cannell, J.Am.Chem.Soc., 94 (1972) 6867.
24. L.G.Cannell, U.S. 3,692,854 (1972); C.A. 77 (1972) 139468s.
25. L.G.Cannell, Ann. N.Y.Acad.Sci., (1973) 143.
26. V.M.Vdovin, A.B.Amerik, V.A.Poletaev, Izv.Akad.Nauk SSSR, Ser. Khim., (1978) 2781.
27. A.B.Amerik, In: Novye aspekty neftekhimitcheskogo sinteza, Inst. Neftekhim.Sint. im. Toptchieva Akad.Nauk SSSR, Moscow, (1978)28.
28. A.B.Amerik, Dissertatsiya, Moscow, 1983.
29. A.Stockis, R.Hoffman, J.Am.Chem.Soc., 102 (1980) 2952.
30. F.W.Hoower, R.V.Lindsey, J.Org.Chem., 34 (1969) 3051.
31. G.Ingrosso, M.Iqbal, R.Rossi, L.Porry, Chim.Ind.(Milan), 55 (1973) 540.
32. P.Binger, U.Schuchardt, Chem.Ber., 113 (1980) 1063.

33. F.N.Jones, R.V.Lindsey, J.Org.Chem., 33 (1968) 3838.

34. S.Otsuka, A.Nakamura, H.Minamida, J.Chem.Soc., Chem.Commun., (1969) 191.

35. S.Otsuka, A.Nakamura, K.Tani, S.Ueda, Tetrahedron Lett., 5 (1969) 297.

36. J.P.Scholten, H.J.Ploeg, Tetrahedron Lett., 13 (1972) 1683.

37. Y.Inoue, Y.Itoh, H.Hashimoto, Chem.Lett., (1978) 911.

38. S.Vatanathan, M.F.Farona, J.Mol.Catal., 7 (1980) 403.

39. S.Vatanathan, M.F.Farona, J.Catal., 61 (1980) 540.

40. U.M.Dzhemilev, R.I.Khusnutdinov, N.A.Shchadneva, O.M.Nefedov, G.A.Tolstikov, Azv.Akad.Nauk SSSR, Ser.Khim., (1989) 2383.

41. G.A.Chukhadzhyan, G.I.Abramyan, G.M.Tonyak, L.I.Sagradyan, T.S.Elbakyan, Zh.Org.Khim., 17 (1981) 1831.

42. I.J.Pasto, D.K.Mitra, J.Org.Chem., 47 (1982) 1381.

43. M.Iyoda, Sh.Tanaka, M.Oda, J.Chem.Soc., Chem.Commun., (1985) 1058.

44. M.Iyoda, Sh.Tanaka, H.Otani, T.Yamauchi, Y.Kuwatani, M.Oda, 5th International Symposium on Homogeneous Catalysis. Program and Abstracts, Kobe, Japan (1986) 272.

45. L.Sthehling, G.Wilke, Angew.Chem., 97 (1985) 505.

46. L.Hogelee, R.West, T.Calabrese, I.Norman, J.Am.Chem.Soc., 101 (1979) 4888.

47. B.Hagenbruch, K.Hesse, S.Heinig, G.Klug, J.Leibigs Ann.Chem., (1981) 256.

48. P.Binger, Angew.Chem., 84 (1972) 352.

49. P.Binger, Angew.Chem.Int.Ed.Engl., 11 (1972) 309.

50. P.Binger, Synthesis, (1973) 427.

51. P.Binger, A.Brinkmann, J.McMeeking, J.Liebigs Ann.Chem., (1977) 1065.

52. P.Binger, M.J.Doyle, R.Benn, Chem.Ber., 116 (1983)1.

53. P.Binger, A.Germer, Chem.Ber., 114 (1981) 3325.

54. R.Noyori, T.Odagi, H.Takaya, J.Am.Chem.Soc., 92 (1970) 5780.

55. P.Binger, A.Brinkmann, P.Wedemann, Chem.Ber., 116 (1983) 2920).

56. P.Binger, A.Brinkmann, W.J.Richter, Tetrahedron Lett., 24 (1983) 3599.

57. R.Noyori, Y.Kumagai, I.Umeda, H.Takaya, J.Am.Chem.Soc., 94(1972) 4018.

58. R.Noyori, M.Yamakawa, Tetrahedron Lett., 19 (1978) 4823.
59. P.Binger, P.Wedemann, Tetrahedron Lett., 29 (1978) 1045.
60. H.M.Buch, G.Schroth, R.Mynott, P.Binger, J.Organomet.Chem., 247 (1983) C63.
61. P.Binger, P.Wedemann, Tetrahedron Lett., 24 (1983) 5847.
62. P.Binger, Q.-H.Lü, P.Wedemann, Angew.Chem., 97 (1985) 333.
63. P.Binger, U.Schuchardt, Chem.Ber., 114 (1981) 3313.
64. P.Binger, P.Bentz, Angew.Chem., 94 (1982) 636.
65. A.Germer, Dissertation, Ruhr-Universität, Bochum, 1978.
66. B.M.Trost, Tetrahedron 33 (1977) 2615.
67. B.M.Trost, D.M.Chan, J.Am.Chem.Soc., 105 (1983) 2315.
68. B.M.Trost, P.Renaut, J.Am.Chem.Soc., 104 (1982) 6668.
69. B.M.Trost, D.M.T.Chan, J.Am.Chem.Soc., 101 (1972) 6429.
70. I.Shimizu, Y.Ohashi, J.Tsuji, Tetrahedron Lett., 25 (1984) 5183.
71. B.M.Trost, T.N.Nanninga, T.Satoh, J.Am.Chem.Soc., 107 (1985) 721.
72. B.M.Trost, B.P.Copolla, J.Am.Chem.Soc., 104 (1982) 6879.
73. B.M.Trost, D.M.T.Chan, J.Am.Chem.Soc., 104 (1982) 3733.
74. B.M.Trost, Angew.Chem., 98 (1986) 1.
75. R.Köster, S.Arora, P.Binger, J.Liebigs Ann.Chem., (1973) 1219.
76. A.J.Shipperijn, J.Lukas, Tetrahedron Lett., 13 (1972) 231.
77. A.J.Shipperijn, J.Lukas, Recl.Trav.Chim.Pays-Bas, 92 (1973) 572.
78. P.Binger, H.Schafer, Tetrahedron Lett., 16 (1975) 4673.
79. O.M.Nefedov, I.E.Dolgii, E.V.Bulusheva, A.Ya.Shteinshneider, Izv.Akad.Nauk SSSR, Ser.Khim., (1976) 1901.
80. I.J.Weigert, R.L.Baird, J.R.Schapley, J.Am.Chem.Soc., 92 (1970) 6630.
81. M.L.Deem, Synthesis, (1972) 675.
82. P.Binger, J.McMeeking, Angew.Chem., 86 (1974) 518.
83. P.Binger, A.Brinkmann, Chem.Ber., 111(1978) 2689.
84. P.Binger, J.McMeeking, U.Schuchardt, Chem.Ber., 113 (1980) 2372.
85. P.Binger, U.Schuchardt, Chem.Ber., 114 (1981) 1649.
86. P.Binger, U.Schuchardt, Angew.Chem., 87 (1975) 715.
87. N.M.Tsvetkova, Dissertatsija, Moskow, 1986.

88. P.Binger, M.J.Doyle, J.McMeeking, C.Kruger, Y.-H.Tsay, J.Organomet.Chem., 135 (1977) 405.
89. P.Binger, H.M.Buch, R.Benn, R.Mynott, Angew.Chem., 94 (1982) 66.
90. M.I.Doyle, J.McMeeking, J.Chem.Soc., Chem.Commun., (1976) 376.
91. B.Cetinkaya, P.Binger, C.Krüger, Chem.Ber., 115 (1982) 3414.
92. P.Binger, B.Cetinkaya, M.I.Doyle, A.Germer, U.Schuchardt, Fundam.Res.Homogeneous Catal., 3 (1979) 271.
93. P.Binger, M.I.Doyle, J.Organomet.Chem., 162 (1978) 195.
94. T.A.Peganova, P.V.Petrovskii, L.S.Isaeva, D.N.Kravtsov, D.B. Furman, A.V.Kudryashev, A.O.Ivanov, S.V.Zotova, O.V.Bragin, J.Organomet.Chem., 282 (1985) 283.
95. P.Binger, J.McMeeking, H.Schafer, Chem.Ber., 117 (1984) 1551.
96. Yu.V.Tomilov, V.G.Bordakov, N.M.Tsvetkova, A.Ya.Shteinshneider, I.E.Dolgii, O.M.Nefedov, Izv.Akad.Nauk SSSR, Ser.Khim., (1983) 336.
97. Yu.V.Tomilov, V.G.Bordakov, I.E.Dolgii, O.M.Nefedov, U.S.S.R. 891,608 (1981); C.A. 96 (1982) 199161p.
98. H.Takada, M.Yamakawa, N.Noyori, Bull.Chem.Soc. Japan, 55 (1982) 852.
99. R.L.Preuett, E.A.Rick, U.S. 3,440,294 (1969); C.A. 71 (1969) 3056z.
100. D.E.Applequist and D.C.England, U.S. 2,940,984 (1969); C.A. 54 (1960) 19539f.
101. L.G.Cannell, U.S. 3,271,438 (1966); C.A. 65 (1966) 16881h.
102. C.D.Weis and A.C.Rochat, German 1,931,152 (1970); C.A. 72 (1970) 66495d.
103. H.K.Myers and A.Schneider, U.S. 4,107,198 (1978); C.A. 90 (1979) 86877j.
104. A.Schneider, H.K.Myers, U.S. 4,139,714 (1979); C.A. 90 (1979) 168158q.
105. H.K.Myers, U.S. 4,139,715 (1979); C.A. 90 (1979) 168159r.
106. A.Schneider, H.K.Myers, U.S. 4,142,055 (1979); C.A. 90 (1979) 168160j.
107. S.Yoshikawa, C.Aoki, J.Furukawa, Bull.Chem.Soc. Japan, 48 (1975) 3239.
108. G.N.Schrauzer, S.Eichler, Chem.Ber., 97 (1964) 2451.

109. G.N.Schrauzer, S.Eichler, Chem.Ber., 95 (1962) 2764.

110. R.Noyori, I.Umeda, H.Kawauchi, H.Takaya, J.Am.Chem.Soc., 97 (1975) 812.

111. M.Catellani, G.P.Chiusoli, E.Dradi, G.Salerno, J.Organomet. Chem., 177 (1979) C29.

112. U.M.Dzhemilev, R.I.Khusnutdinov, D.K.Galeev, O.M.Nefedov, G.A.Tolstikov, Izv.Akad.Nauk SSSR, Ser.Khim., (1987) 138.

113. U.M.Dzhemilev, R.I.Khusnutdinov, D.K.Galeev, G.A.Tolstikov, Tez.dokl. VI Vsesoyuzn. konf. "Katalititcheskie reaktsii v zhidkoi faze", Alma-Ata, Ch.2 (1983) 195.

114. U.M.Dzhemilev, R.I.Khusnutdinov, D.K.Galeev, G.A.Tolstikov, Tez. dokl. III Vsesoyuzn. konf. pometalloorganitcheskoi khimii, Ufa, Ch.2 (1985) 153.

115. U.M.Dzhemilev, R.I.Khusnutdinov, D.K.Galeev, G.A.Tolstikov, Izv.Akad.Nauk SSSR, Ser.Khim., (1987) 154.

116. R.D.Coulson, J.Org.Chem., 37 (1972) 1253.

117. R.D.Coulson, U.S. 3,760,016 (1973); C.A. 80(1973) 60796a.

118. A.Greco, A.Carbonaro, G.Dall'Asta, J.Org.Chem., 35 (1970) 271.

119. S.P.A.Montedison, Italy 875,512 (1970); C.A. 83 (1975) 27724q.

120. U.M.Dzhemilev, R.I.Khusnutdinov, Z.S.Muslimov, G.A.Tolstikov, Izv.Akad.Nauk SSSR, Ser.Khim., (1988) 13.

121. U.M.Dzhemilev, R.I.Khusnutdinov, V.A.Dokitchev, Z.S.Muslimov, I.E.Dolgii, G.A.Tolstikov, O.M.Nefedov, Ref.dokl. i soobshch. XII Mendeleevskogo s'ezda po obshchei i prikl. khimii, Moscow, Izd. Nauka, Ch.2 (1981) 8.

122. U.M.Dzhemilev, R.I.Khusnutdinov, Z.S.Muslimov, O.M.Nefedov, G.A.Tolstikov, Tez.dokl. VI Vsesoyuzn. konf. "Katalititcheskie reaktsii v zhidkoi faze", Alma-Ata, Ch.2 (1983) 194.

123. Z.S.Muslimov, Dissertatsija, Ufa, 1988.

124. T.A.Mitsudo, K.Kokuryo, Y.Takegami, J.Chem.Soc., Chem.Commun., (1976) 722.

125. T.A.Mitsudo, K.Kokuryo, T.Shinsugi, Y.Nakagawa, Y.Watanabe, Y.Takegami, J.Org.Chem., 44 (1979) 4492.

126. R.N.Warrener, J.G.Pitt,D.N.Butler, J.Chem.Soc., Chem.Commun., (1983) 1340.

127. J.E.Lyons, H.K.Myers, A.Schneider, J.Chem.Soc., Chem.Commun., (1978) 636.

128. J.E.Lyons, H.K.Myers, A.Schneider, J.Chem.Soc., Chem.Commun., (1978) 638.

129. H.K.Myers, J.E.Lyons, A.Schneider, U.S. 4,110,409 (1978); C.A. 90 (1979) 86878k.

130. J.E.Lyons and A.Schneider, U.S. 4,132,742 (1979); C.A. 90 (1979) 121160u.

131. U.M.Dzhemilev, R.I.Khusnutdinov, Z.S.Muslimov, G.A.Tolstikov, Izv.Akad.Nauk SSSR, Ser.Khim., (1987) 1061.

132. Shell International Research Maatschappij N.V., Neth.Appl. 6,504,000 (1965); C.A. 64 (1966) 8057a.

133. A.Carbonaro, F.Cambisi, G.Dall'Asta, J.Org.Chem., 36 (1971) 1443.

134. H.K.Myers, J.Lyons, A.Schneider, U.S. 4,190,610 (1980); C.A. 90 (1980) 28782a.

135. H.K.Myers, J.Lyons, A.Schneider, U.S. 4,100,216 (1978); C.A. 90 (1979) 22439k.

136. H.K.Myers, J.E.Lyons, A.Schneider, U.S. 4,190,610 (1980); C.A. 93 (1980) 28782a.

137. T.Inukai, A.Takahashi, J.Chem.Soc., D, (1970) 1473.

138. Montedison S.P.A., Italy 875,513 (1970); C.A. 83 (1975) 27723p.

139. P.Heimbach, P.V.Myer, G.Wilke, J.Liebigs Ann.Chem., (1975)743.

140. Y.Ishii, M.Kawahara, T.Noda, H.Jcligaki, M.Ogawa, Bull.Chem. Soc. Japan, 56 (1983) 2181.

141. S.Yoshikawa, S.Nishimura, J.Kiji, J.Furukawa, Tetrahedron Lett., 14 (1973) 3071.

142. J.Kiji, S.Yoshikawa, E.Sasakawa, S.Nishimura, J.Furukawa, J.Organomet.Chem., 80 (1974) 267.

143. J.Furukawa, J.Kiji, Organotransition-Metal Chemistry, New-York-London, 1975, 119.

144. C.A.Tolman, J.Am.Chem.Soc., 92 (1970) 6777.

145. M.C.Gallazzi, T.L.Hanlon, G.Vitulli, L.Porri, J.Organomet. Chem., 33 (1971) C45.

146. R.Noyori, T.Ishigami, N.Hayashi, H.Takaya, J.Am.Chem.Soc., 95 (1973) 1674.

147. P.Binger, U.Schuchardt, Angew.Chem., 98 (1977) 254.

148. P.Binger, U.Schuchardt, Chem.Ber., 113 (1980) 3334.
149. P.Binger, U.Schuchardt, Ger.Offen. 2,707,879 (1978); C.A. 89 (1978) 214995q.
150. P.Binger, P.Bentz, J.Organomet.Chem., 221 (1981) C33.
151. P.Bentz, Dissertation, Universität Kaiserslautern, 1982.
152. I.E.Dolgii, Yu.V.Tomilov, N.M.Tsvetkova, V.G.Bordakov, O.M. Nefedov, Izv.Akad.Nauk SSSR, Ser.Khim., (1983) 958.