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Invited Review

Transition metal complexes in the chemistry of vinylcyclopropanes

R.I. Khusnutdinov and U.M. Dzhemilev

Institute of Petrochemistry and Catalysis, Bashkirian Academy of Sciences, Bashkortostan, Ufa, 450075 (Russian Federation)

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1. Introduction

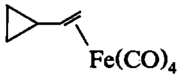
The special structure of the cyclopropane ring confers on it an unusually strong tendency to conjugate with a double bond. This is due to internal strain that imparts distinctive *p*-characteristics to the compound. A 1,3-dienic system is modeled by coupling of cyclopropane to an olefin or acetylene, and this was clearly confirmed by photoelectron spectroscopy [1,2], and electron diffraction [3] and also by a lot of the chemical reactions [4]. Thus, vinylcyclopropane (VCP) and its substituted derivatives show promising and interesting transformations catalyzed by transition metal complexes (TMC). Sarel and his coworkers carried out the first research in this field [4,6–9] with studies on the reactions of VCP with iron carbonyl complexes which were summarized in a comprehensive review published in 1978 [4]. Subsequently the TMC catalyzed reactions of VCP aroused strong interest in many laboratories and new catalysts were used for an extended range of VCPs, including those with electron-withdrawing substituents, cyclopropyl-substituted 1,3-dienes and acetylenes.

The principal objective of this review is to consider and systematize the reported information on stoichiometric and catalytic reactions of VCP and related molecules with transition metal complexes.

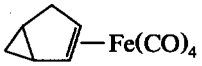
2. Catalysis by iron complexes

Most of the known $Fe_n(CO)_m$ catalyzed reactions were carried out with stoichiometric amounts of $Fe(CO)_5$, $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$. The reactions often led to complexation that was sometimes preceded by isomerization of the cyclopropane ring (CPR). The transformations were subdivided into five types [4]:

(i) creation of π-complexes **1**, **2** via interaction of the VCP vinyl group with the central Fe atom [4–7];

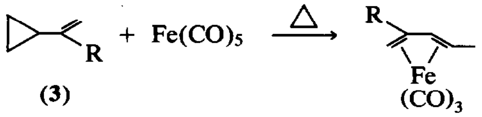


(1)



(2)

(ii) isomerization of VCP **3** into 1,3-dienes by opening of the CPR and formation of a Fe η^4-diene complex **4** [8–10];



(3) **(4)**

(iii) photoinitiated 1,5-carbonylation of VCP in the presence of $Fe(CO)_5$, resulting in cyclohexenones **5**

Correspondence to: Professor U.M. Dzhemilev.

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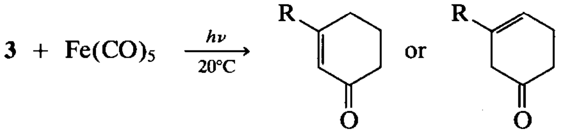
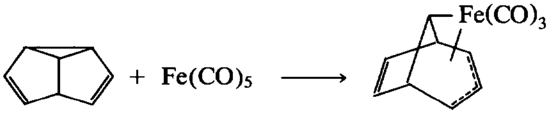
and **6** (under UV light; the Fe complex generates CO that is necessary for the reaction) [11,12];



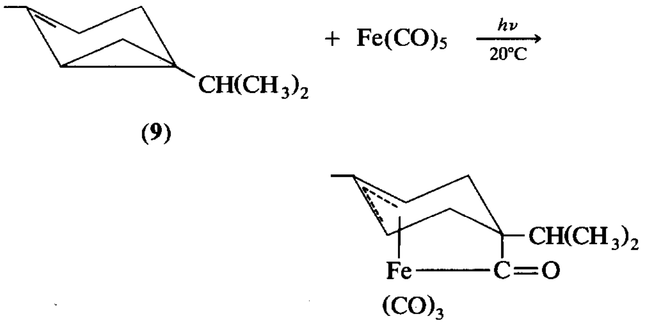
(5) **(6)**

(iv) formation of a Fe σ,π-allylic complex **8** by insertion of the metal atom into the CPR through a C–C bond [13];



(7) **(8)**

(v) simultaneous insertion of the carbonyl group and the iron atom into the VCP structure, resulting in a metal acyl complex **10** under UV light.

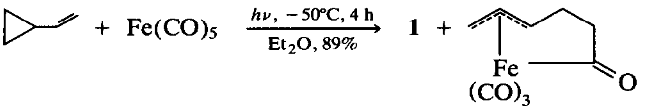


(9)

(10)

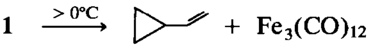
In this complicated series of VCP transformations assisted by homogeneous metal-complexed catalysts, the key step is the coordination of the double bond at the central metal atom. This is supported by the observation that dicyclopropylketone and cyclopropylbenzene are inert towards Fe complexes: no double bonds are present, though the three-membered rings are conjugated with the carbonyl group or the aromatic ring [4,12,17].

The formation of the π-complex **1** with Fe compounds was described first for VCP itself [5]. The complex **1** is unstable under ambient conditions, and can be detected only at −50°C [4,5].

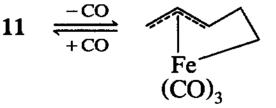


(11)

At 0°C, the complex **1** decomposes to give the starting monomer and $Fe_3(CO)_{12}$ [5].

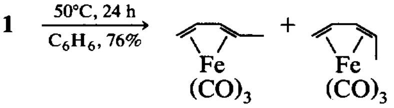


The second complex **11** in the reaction, is stable under CO at 25°C for several hours, whilst in the absence of free carbon oxide it is readily transformed into a σ,π-allylic complex **12** with loss of CO.



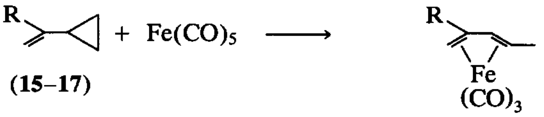
(12)

However, under heating in a sealed tube, the complex **1** is isomerized into a mixture of the penta-1,3-diene iron tricarbonyl complexes **13** and **14**, and not the acyl derivative **11**. Therefore, one may assume that **13** and **14** are created *via* some competing reactions of VCP with different iron complexes formed by photolysis of an ether solution of $Fe(CO)_5$ [5].



(13) 3:1 **(14)**

Diene complexes **18–20** were also found from reactions of the aryl-substituted VCP **15–17** with $Fe(CO)_5$, although rather rigorous conditions are necessary (140°C, 10 h) to obtain **18–20** [8,9].



(15–17)

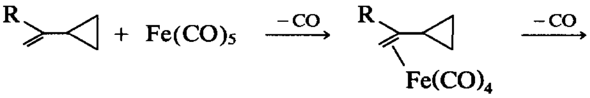
R = Ph **(18)**
p-ClC_6H_4 **(19)**
p-$MeOC_6H_4$ **(20)**

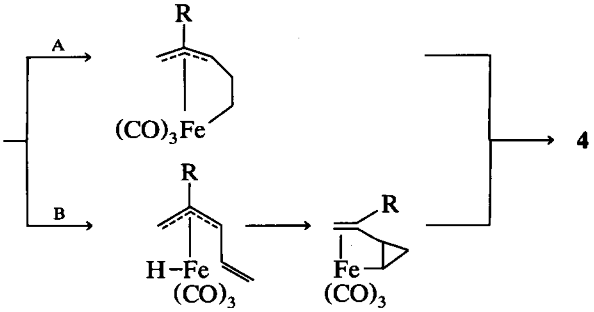
Sarel *et al.* suggested a mechanism for the formation of the diene complexes **18–20**, which includes the following key steps [8,9]:

(i) opening of the CPR *via* the two alternative routes A and B;

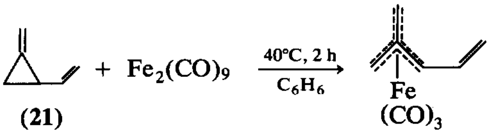
(ii) hydride shift;

(iii) formation of the Fe complex **4** with the 1,4-diene obtained by ring opening.



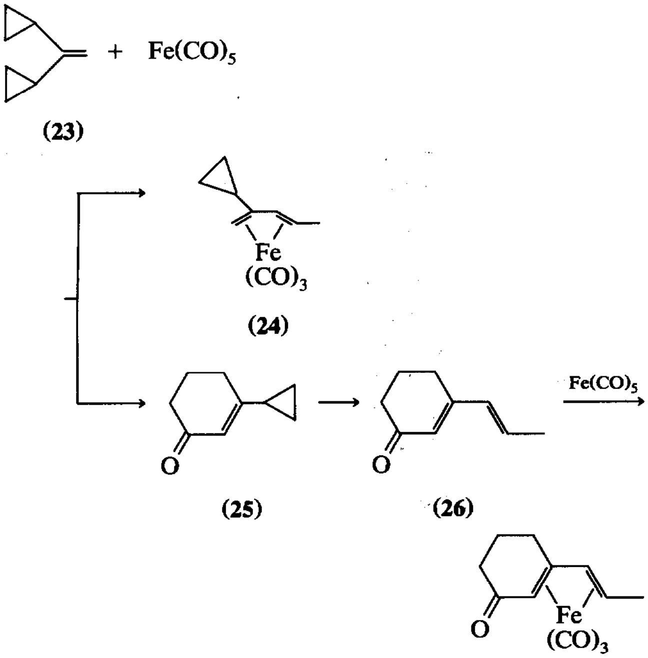


1-Methylene-2-vinylcyclopropane **21** reacts differently from VCP. The vinyl group is not involved in the reaction, and it appears more thermodynamically advantageous to form a Fe trimethylene-methane complex **22** [14,15].



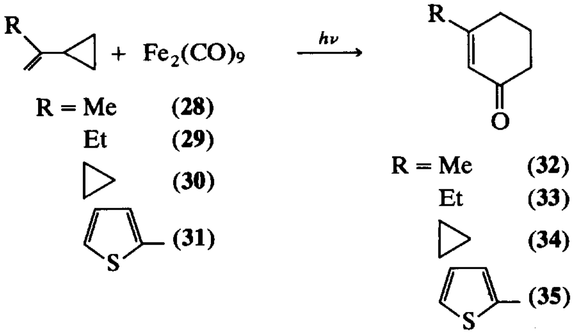
(21) **(22)**

1,1-Dicyclopropylethylene **23** also reacts in unusual way with $Fe(CO)_5$. In addition to the expected complex **24**, the reaction also gives the complex **27** of the dienone **26**. The attempts of Snarl, Kelly *et al.* to prepare **27** by heating the diene complex **24** were fruitless; **27** thus appears to be formed by an independent route, *i.e.* through enone **26** [9,16].



(23) **(24)** **(25)** **(26)** **(27)**

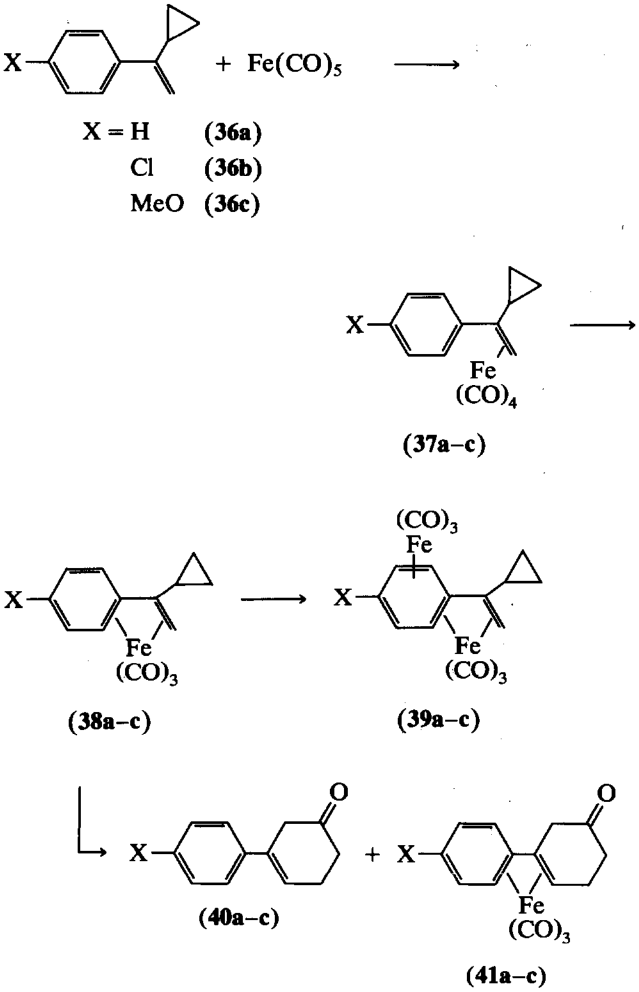
Enones like **25** are the main products in the UV-activated reactions of VCP with $Fe_2(CO)_9$ [12].



R = Me **(28)**
Et **(29)**
cyclopropyl **(30)**
2-thienyl **(31)**

R = Me **(32)**
Et **(33)**
cyclopropyl **(34)**
2-thienyl **(35)**

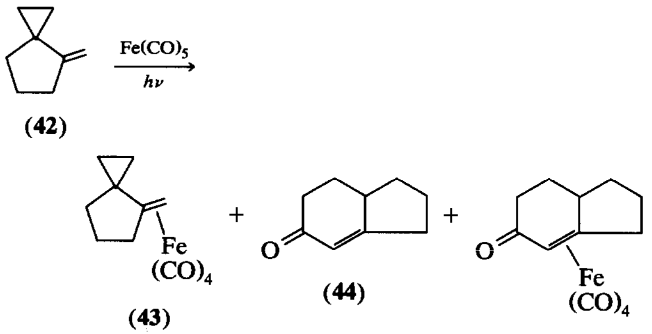
α-Cyclopropylstyrenes yielded complexes **38** + **39a–c**, **41a–c** and enones **40a–c** [17].



X = H **(36a)**
Cl **(36b)**
MeO **(36c)**

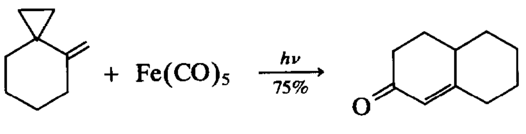
(37a–c) **(38a–c)** **(39a–c)** **(40a–c)** **(41a–c)**

Sarel *et al.* described the unusual case of the formation of a Fe olefinic complex **45** *via* the enone **44** that results from the reaction of 2-methylenespiro[4.2]-heptane **42** with Fe(CO)$_5$ under photocatalytic conditions [6].

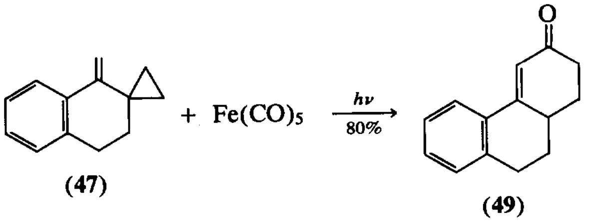


(42) **(43)** **(44)** **(45)**

In contrast to **42**, *spiro*-coupled VCP **46** and **47** under otherwise similar conditions give enones **48** and **49** exclusively [6].



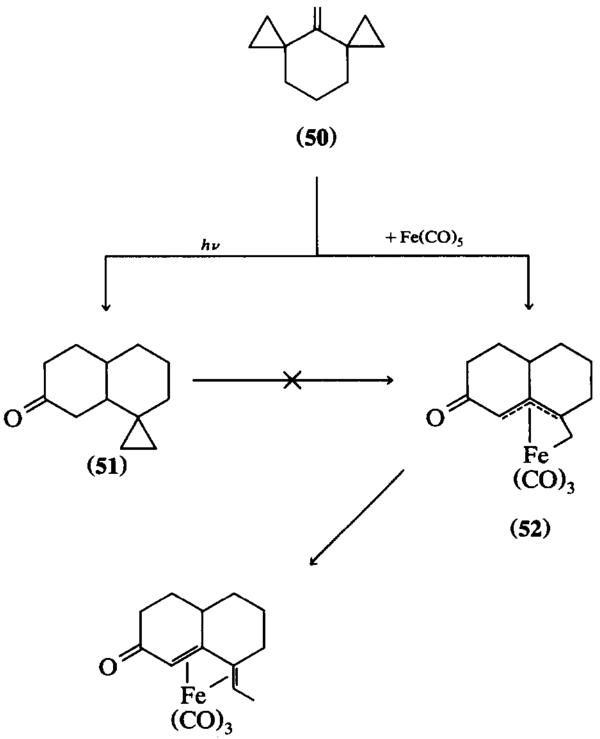
(46) **(48)**



(47) **(49)**

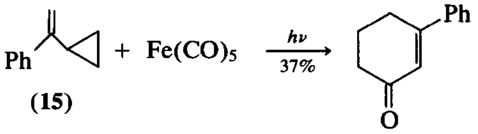
The reaction of dispiro[2.1.2.3]decane **50** which contains two cyclopropane groups, is not complete at the step of **51**, but it continues to lead to two complexes **52** and **53**, major and minor, respectively.

Sarel *et al.* provided evidence that the complex **53** arises through the intermediate **51**, while the σ,π-allylic complex **52** is formed independently, but the details of the reaction mechanism remain vague [4,6].



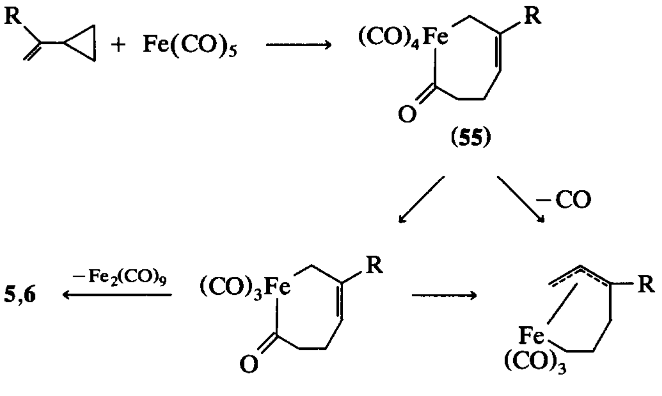
(50) **(51)** **(52)** **(53)**

1-Phenyl-1-cyclopropylethylene **15** gives also an enone **54** under photolysis, but the yield is low [18].



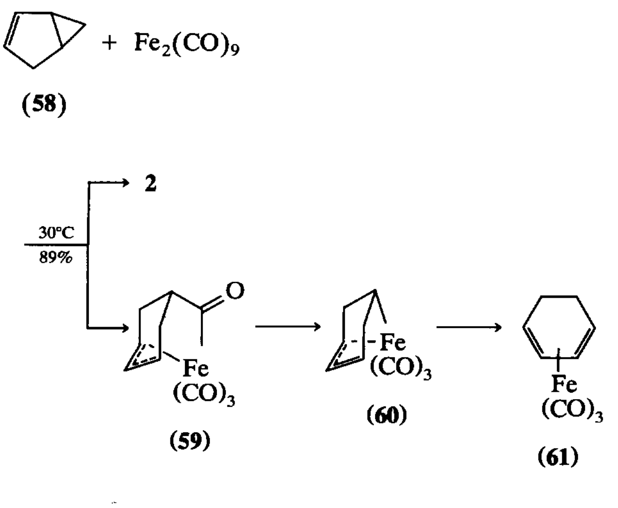
(15) **(54)**

Aumann *et al.* reported an in-depth analysis of the mechanism of formation of the enones [5] and provided a rational explanation for both the transformations discussed in this paper and indeed all types of the VCP reactions with Fe carbonyls. Great importance was attributed to the reaction of 1,5-cycloaddition of the Fe carbonyl moiety Fe=C=O to the conjugated structure of VCP, giving two intermediates **55** and **56** with Fe cycloheptenone structure. These intermediates were labile, but could be identified unambiguously by spectroscopic techniques. Subsequent transformations of **55** and **56** may give either the enones **5** and **6** or a Fe σ,π-allylic complex **57**, according to the following scheme [4,5]:

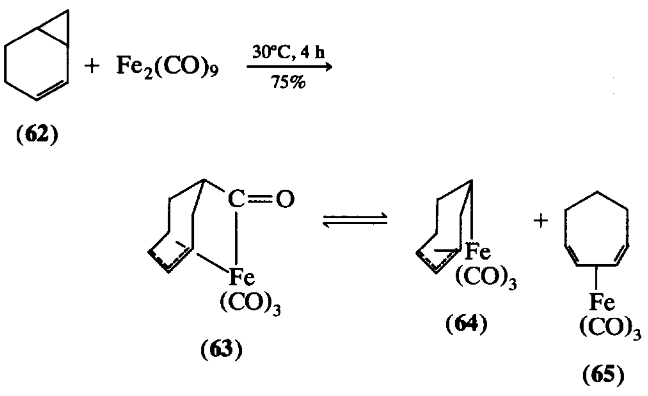


This scheme demonstrates the close relation of the reaction routes of VCP with $Fe(CO)_5$ and $Fe_2(CO)_9$. Thus, the σ,π-allylic complex **57** and the Fe acyl complexes **55** and **56** can interconvert. It should be emphasized here that the reactions resulting in the σ,π-allylic and metal acyl complexes are peculiar for polycyclic VCP, particularly for strained VCPs with cage structures. The resultant complexes are more stable than the starting VCPs which have strained bridging structures. This provides for better interaction of the reaction centres in the intermediate and final products, because of their steric juxtaposition.

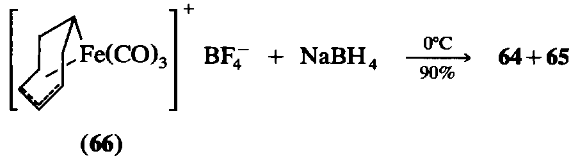
The reaction of the bicyclic VCP **58** with $Fe_2(CO)_9$, is somewhat unusual in giving two complexes **2** and **59** in a 1 : 10 ratio. When **59** is heated in decane solution, it isomerizes into the diene complex **61**, most likely through the intermediate **60** [7].



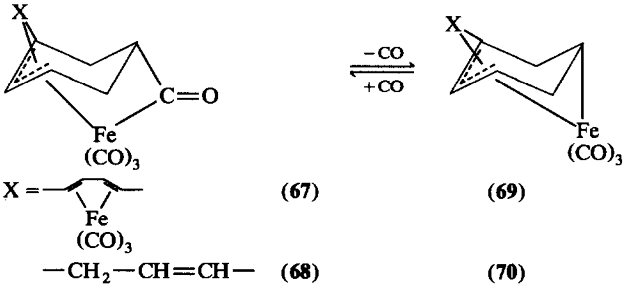
Bicyclo[4.1.$0^{1,6}$]hept-2-ene **62** reacts with $Fe_2(CO)_9$ in a similar way [7].



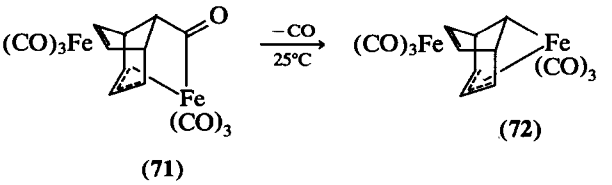
The structures of **64** and **65** were confirmed by preparing them from the reaction of the cationic complex **66** with $NaBH_4$ in water at 0°C [7].



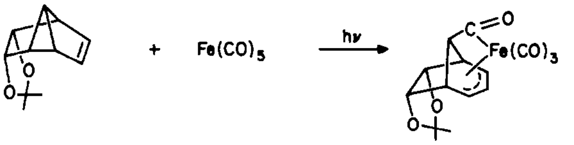
Note that an equilibrium often exists between the metal acyl- and σ,π-allyl-structures of the Fe carbonyl complexes of VCP. Thus, metal acyl complexes **67** and **68** in boiling hexane, quantitatively eliminate CO and transform into σ,π-allylic complexes **69** and **70**, respectively. Treatment of the solutions of **69** and **70** with free carbon oxide at 25°C, regenerate the metal acyl complexes **67** and **68**, respectively [7].



Another metal acyl complex **71** is rather stable at low temperatures, while it spontaneously and irreversibly liberates CO at 25°C to give the σ,π-allylic derivative **72** [7].

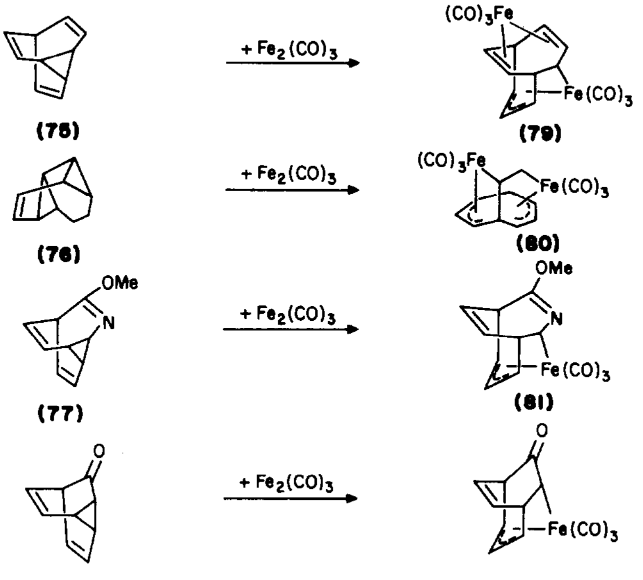


It is interesting that Scharf *et al.* obtained the stable metal acyl complex **74** from the reaction of *endo*-6,7-dihydroxy-6,7-dihydrosemibullvalene acetonide **73** with $Fe(CO)_5$ [19].



(73) **(74)**

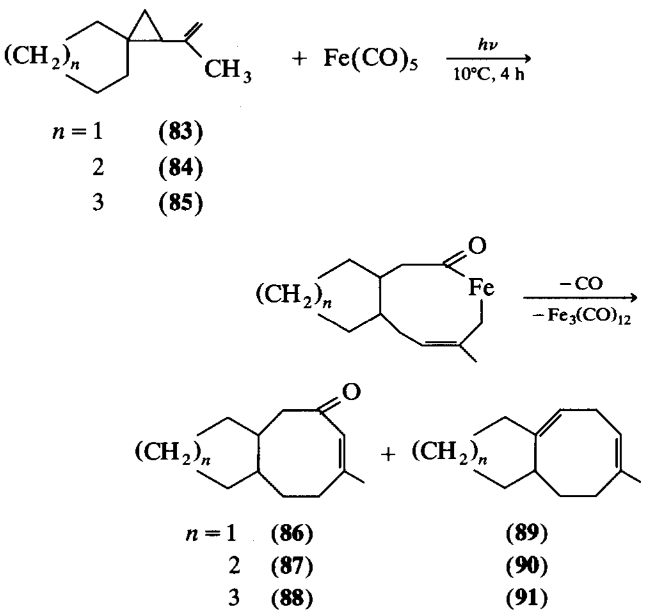
Almost all of the known VCPs having cage-like structures react similarly with $Fe(CO)_5$. The most interesting are the σ,π-allylic complexes obtained in the reactions of bullvalene **75** [20–22], isobullvalene **76** [23,24], azabullvalene **77** [25], and barbaralone **78** [26].



(75) **(79)** **(76)** **(80)** **(77)** **(81)** **(78)** **(82)**

Similar transformations are known to occur during the reactions of semibullvalene [13,27,28], homosemibullvalene [26], norcaradiene [29], and dibenzosemibullvalene [30–33].

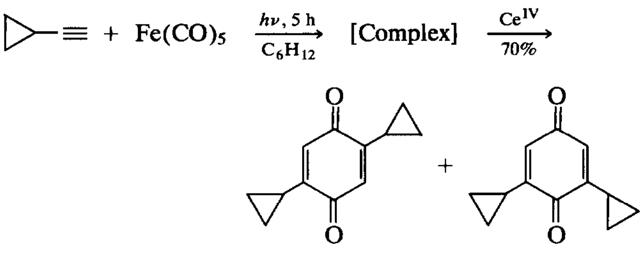
Sarel *et al.* described the unusual reaction of cheletropic 1,7-addition of carbon oxide generated from $Fe(CO)_5$, to VCP [34–36]. The starting VCPs **83**, **84** and **85** each contained a divinylcyclopropane fragment with a *spiro*-coupled CPR. Photochemical transformations of **83–85** with $Fe(CO)_5$ led to high yields of isomeric cyclooctadienones **86–91**. Alternative synthetic routes to **86–91** are complicated [34–36].



$n = 1$ **(83)**
2 **(84)**
3 **(85)**

$n = 1$ **(86)** **(89)**
2 **(87)** **(90)**
3 **(88)** **(91)**

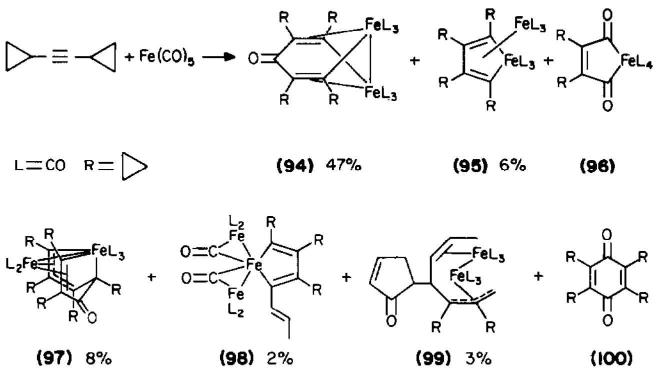
It is noteworthy that cyclopropyl-substituted acetylenes also form complexes with Fe carbonyls. Thus the reaction of cyclopropylacetylene with $Fe(CO)_5$ under UV light gives a complex of unidentified structure, which is oxidized to the isomeric quinones **92** and **93** [37]. The structures of **92** and **93** imply that at least two molecules of cyclopropylacetylene and two moles of carbon dioxide are involved in the reaction.



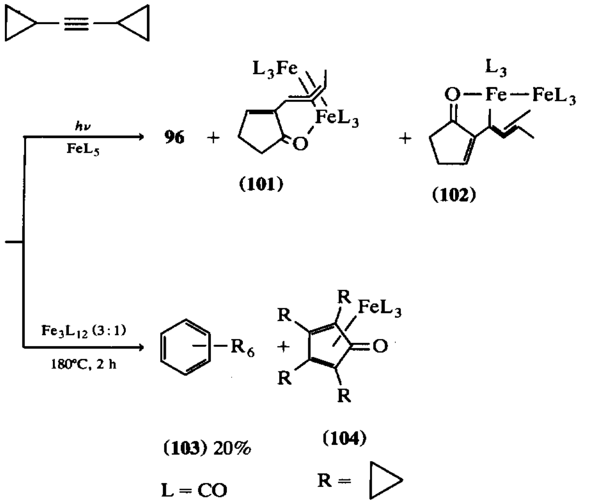
(92) **(93)**

The reactions of Fe carbonyls with dicyclopropylacetylene (DCPA) show a very intricate pattern [38,39]. In addition to complexation there occur catalytic carbonylation, dimerization, and cyclopropyl-allylic isomerization of the three-membered rings. The compositions and structures of the products depend on both the reaction conditions and the nature of the Fe carbonyl complex. The following scheme shows complexes **94–99** formed in a solution of DCPA and $Fe(CO)_5$ (2 : 1) in cyclohexane under UV light [39].

Boiling a solution of DCPA with $Fe_3(CO)_{12}$ in benzene gives the complexes **95**, **98** and, in principal yield, **99**. Photolysis of DCPA and $Fe(CO)_5$ with a deficiency of acetylene (DCPA : Fe = 1 : 5) gives the two new com-

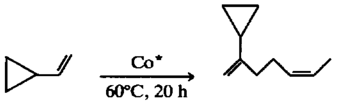


plexes **101** and **102** both incorporating one mole of the acetylene [39]. A high-temperature reaction of DCPA with $Fe_3(CO)_{12}$ (180°C, 2 h) leads not only to complexation but to catalytic trimerization of acetylene into hexacyclopropylbenzene **103** [38].



3. Catalysis by cobalt complexes

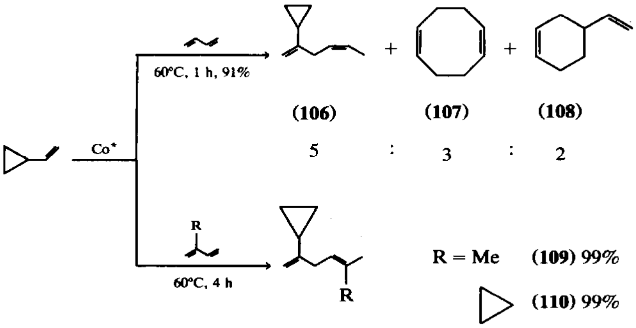
As opposed to the Fe complexes considered in section 2, Co-containing catalysts can give homo- and co-dimerization of VCP and the related species with their three-membered ring. Thus, linear dimerization of VCP with the catalytic system $Co(acac)_3 + Ph_2P(CH_2)_2PPh_2 + AlEt_2Cl$ (1:1.5:12) gave 2-cyclopropylhepta-1,5*Z*-diene **105** [40–42].



(105)

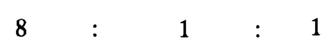
$Co^* = Co(acac)_2 + Ph_2P(CH_2)_2PPh_2 + AlEt_2Cl, C_6H_6$

This same catalyst is highly active in the codimerization of VCP and 1,3-dienes. Moreover, in the reaction of 2-substituted 1,3-dienes it is more selective, giving no homodimers of the dienes [41,42].



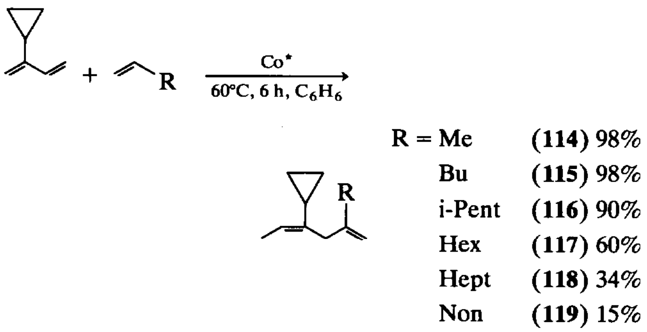
$Co^* = Co(acac)_3 + Ph_2P(CH_2)_2PPh_2 + AlEt_2Cl$

The Co-containing three-component catalysts proved to be effective for linear codimerization of 1- and 2-cyclopropylsubstituted 1,3-dienes with olefins, retaining their CPR. Thus three codimers **111**, **112** and **113** (95% total yield, mole ratio 8:1:1) result from the reaction of 2-cyclopropylbuta-1,3-diene and ethylene in the presence of the catalytic system $Co(acac)_2 + Ph_2P(CH_2)_2PPh_2 + AlEt_2Cl$ (1:1.5:12) [42–44].



$Co^* = Co(acac)_2 + Ph_2P(CH_2)_2PPh_2 + AlEt_2Cl$

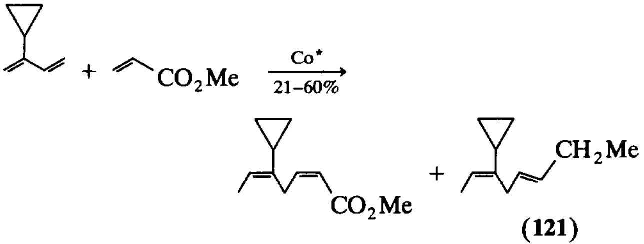
The reactions of 2-cyclopropylbuta-1,3-diene and α-olefins are highly selective in giving to "head-to-tail" linking. The yield of the codimer decreases with a longer alkyl substituent, as a result of lower coordinating ability of the olefin [42].



$Co^* = Co(acac)_2 + PPh_3 + AlEt_2Cl$

The Co-containing catalyst was prepared via reduction of Co(acac)$_2$ with AlEt$_3$.

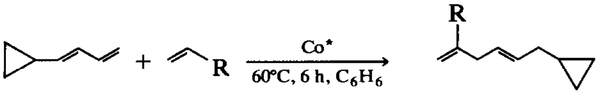
Using the described approach, we succeeded in performing the linear codimerization of 2-cyclopropylbuta-1,3-diene and methyl acrylate, which contains an electron-accepting substituent.



(120) (121)

Co* = Co(acac)$_2$ + PPh$_3$ + AlEt$_3$ (1:1:4), 60°C, 4 h, C$_6$H$_6$

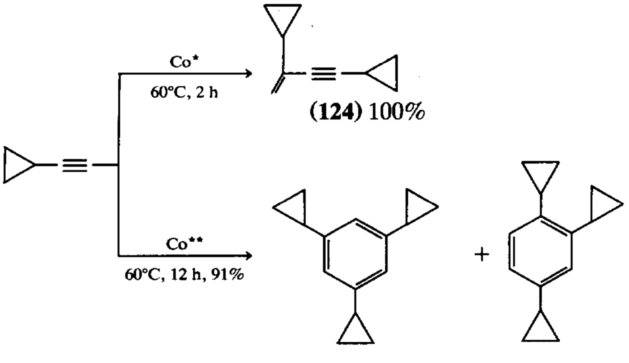
The catalysts based on low-valent cobalt species were usefully employed also for the linear codimerization of 1-cyclopropylbuta-1,3-diene and α-olefins [42,43].



R = H (122) 65%
Me (123) 95%

Co* = Co(acac)$_2$ + Ph$_2$P(CH$_2$)$_2$PPh$_2$ + AlEt$_2$Cl (1:1.5:12)

The three-component Co-containing catalysts proved to be highly effective in linear dimerization and codimerization of cyclopropylacetylene. The reaction route is directed by the nature of the activating ligand in the catalyst. Thus, a linear dimer of cyclopropylacetylene **124** can be obtained selectively with Co(acac)$_2$ + PPh$_3$ + AlEt$_2$Cl (1:1:12, 60°C, 12 h, benzene), whereas isomeric tricyclopropylbenzenes **125** and **126** are the only products when 1,2-bis(diphenylphosphino)ethane is used instead of PPh$_3$ [42,46,47].



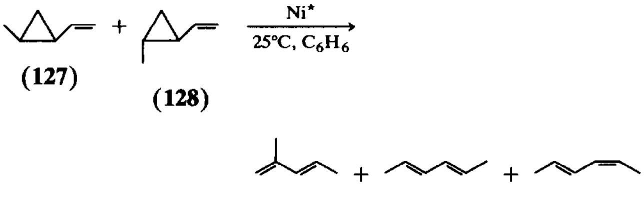
(124) 100%

(125) 9:1 (126)

Co* = Co(acac)$_2$ + PPh$_3$ + AlEt$_2$Cl (1:1:12)
Co** = Co(acac)$_2$ + Ph$_2$P(CH$_2$)$_2$PPh$_2$ + AlEt$_2$Cl (1:2:12)

4. Catalysis by nickel complexes

The literature reports [45–48] that *cis*- and *trans*-methylvinylcyclopropanes **127** and **128** are isomerized in the presence of the catalyst NiCl$_2$ + 2PBu$_3$ + Al(^{i}Bu)$_2$Cl to give a mixture of dienes **129–131**.

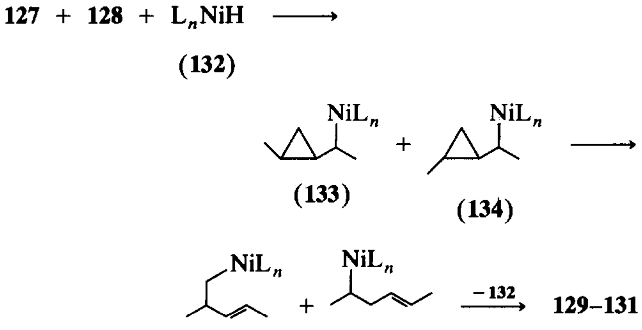


(127) (128)

(129) (130) (131)

Ni* = NiCl$_2$ + 2PBu$_3$ + Al(^{i}Bu)$_2$Cl

It was assumed that a Ni-hydride intermediate **132** is the active catalyst which is responsible for the reaction, because **132** adds to the vinyl groups of VCP **127** and **128**, to give the Ni σ-complexes **133** and **134**. These in their turn are transformed into its final products **129–131** *via* the opening of their three-membered rings and hydride shift [50].

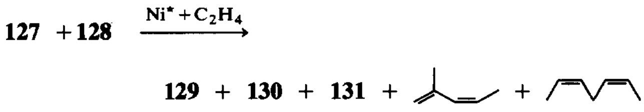


(132)

(133) (134)

(135) (136)

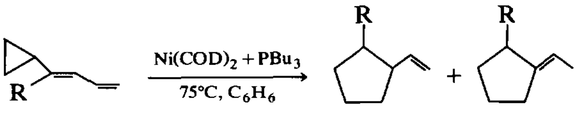
Miller *et al.* [48] found that ethylene promotes the activity of the catalysts. This was explained by the participation of the olefin in the Ni-hydride complex. However, ethylene simultaneously affects the isomerization selectivity, thus promoting the formation of the new diene hydrocarbons **137** and **138** [48,49].



(137) (138)

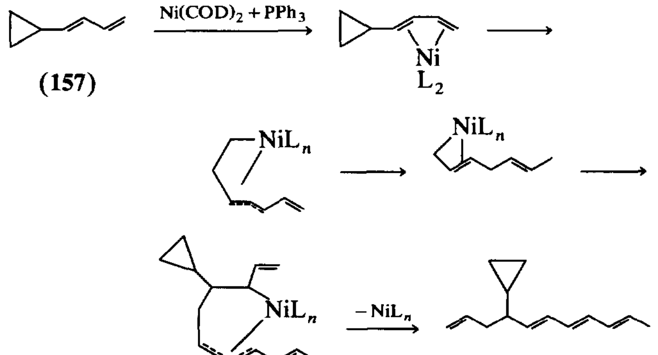
The reaction worked more selectively with the catalyst Ni(C$_2$H$_4$)P(o-CH$_3$–C$_6$H$_4$) + HCl. This system directs the isomerization of **127** and **128** towards the preferable formation of E-piperylene. In this case, larger amounts of ethylene increase appreciably the catalyst's activity [49].

The isomerization of 1-substituted-1-cyclopropylbuta-1,3-dienes **139–144** with a Ni-containing catalyst such as $Ni(COD)_2 + PBu_3$ (COD = 1,5-cyclooctadiene) follows quite a different route leading to vinylcyclopentanes **145–150**. These VCPs are partially transformed into ethylidenecyclopentanes **151–156** due to positional shielding of their double bonds under the reaction conditions [51].



	30–90%	0–25%
R = Me **(139)**	**(145)**	**(151)**
Et **(140)**	**(146)**	**(152)**
^{i}Pr **(141)**	**(147)**	**(153)**
 **(142)**	**(148)**	**(154)**
^{t}Bu **(143)**	**(149)**	**(155)**
Ph **(144)**	**(150)**	**(156)**

The transformation of the simplest 1-cyclopropylbuta-2,3-diene monomer **157** with $Ni(COD)_2 + PPh_3$ is somewhat more complicated [52]. The 4-cyclopropyl-1,5,7,9-undecatriene **158** which is produced may be considered as 1-cyclopropylbuta-1,3-diene dimer. The formation of **158** was assumed to be due to a direct contribution of the three-membered ring to the catalytic process according to the following scheme [52]:

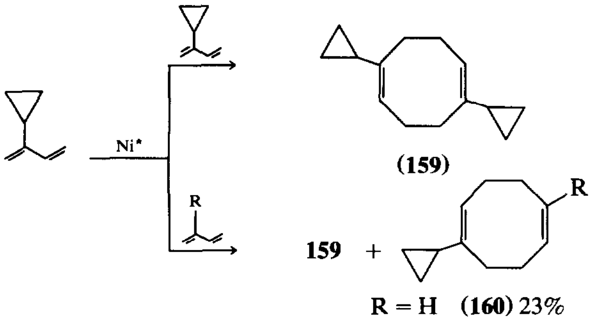


(157)

(158) 50%

L = PPh_3, 1,5-COD

We recently [53] reported the cyclic homo- and codimerization of 2-cyclopropylbutadiene, resulting in cyclopropyl-cycloocta-1,5-dienes. The reactions were assisted by low valent Ni complexes prepared *in situ via* reduction of $Ni(acac)_2$ with $AlEt_3$ in the presence of phosphorus organic ligands as activators. The cyclopropyl fragment was not isomerized during the reaction, as shown in the following scheme:



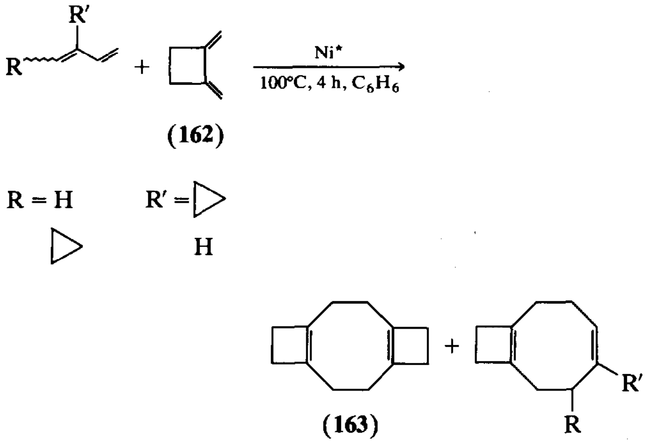
(159)

R = H **(160)** 23%

Me **(161)** 17%

Ni* = $Ni(acac)_2 + P(OPh)_3 + AlEt_3$, 60°C, 5 h

The catalysts are active also in cyclic codimerization of 2- and 1-cyclopropylbuta-1,3-diene and an exotic diene, namely 1,2-dimethylenecyclobutane **162** [45,54, 55].



(162)

(163)

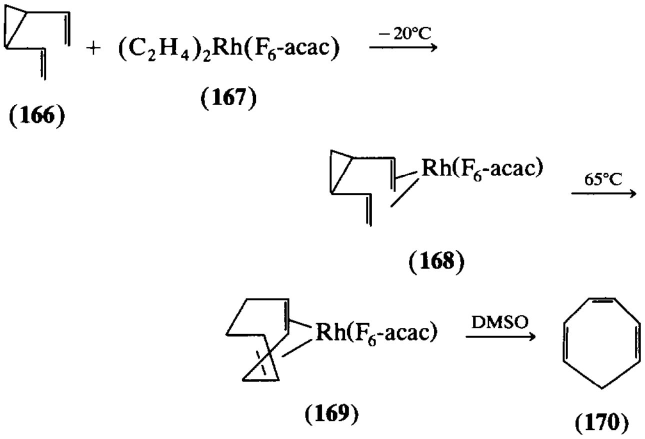
(164) 57%

(165) 29%

Ni* = $Ni(acac)_2 + P(OPh)_3 + AlEt_3$ (1 : 1 : 4)

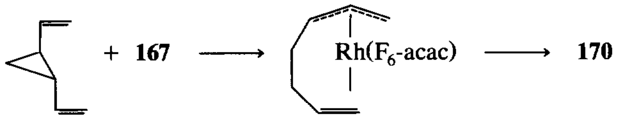
5. Catalysis by rhodium complexes

The reactions of Rh compounds with VCP lead to catalytic transformations or complexation, depending on the VCP structure. The complexation is often preceded by isomerization of the starting VCP into dienes or other species of lower stability [56–61]. Thus, 1,2-*cis*-divinylcyclopropane **166** easily substitutes for the ethylene moiety in a complex such as $(C_2H_4)Rh(F_6\text{-}acac)$ **167** at −20°C to give the related complex **168**. At higher temperature (up to 65°C), **166** is rearranged into cyclohepta-1,4-diene **170** that remains in the coordination sphere of the Rh, and may readily be isolated from **169** via DMSO induced substitution of the ligand.



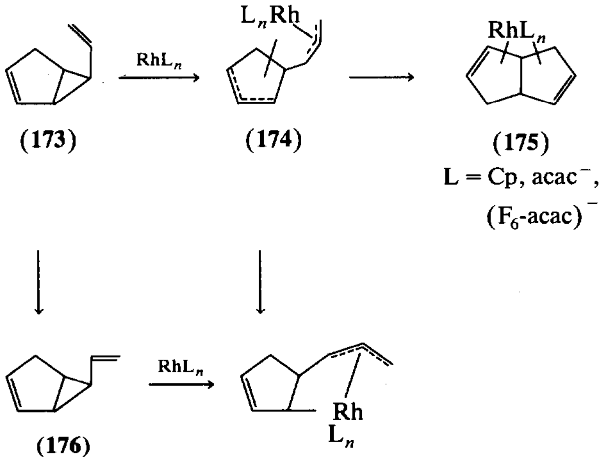
(166) (167) (168) (169) (170)

1,2-*Trans*-divinylcyclopropane **171** enters into a similar reaction with **167**, but gives the bis-π-allylic complex **172**. At 95°C the complex **172** decomposes to give neat cyclohepta-1,4-diene **170**, and at this temperature, the reaction follows a catalytic route.



(171) (172)

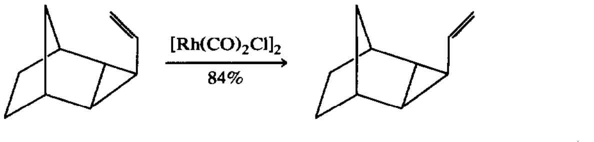
The bicyclic divinylcyclopropanes **173** and **176** undergo similar transformations with Rh complexes. It is noteworthy that both of the divinylcyclopropanes give the same Rh complex **175** with coordinated tetrahydropentalene [61–65].



(173) (174) (175) L = Cp, acac$^-$, (F$_6$-acac)$^-$

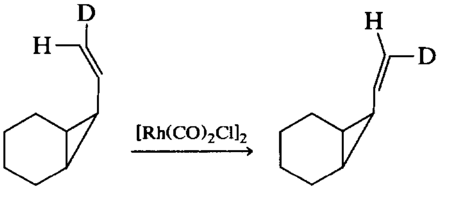
(176) (177)

Two reasons seem plausible so far for the reaction path. Either the complex **174** is more stable than the σ,π-complex **177** or Rh is capable of assisting in the *syn–anti*-isomerization of VCP. The isomerization was performed as a single-step reaction with **178** converted into **179** [65,66].



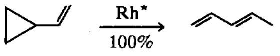
178 (179)

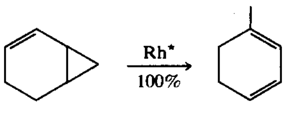
Salomon *et al.* [65] used deuterium as a label and found that the *syn–anti*-rearrangement of the vinyl group took place simultaneously with *E–Z*-isomerization.



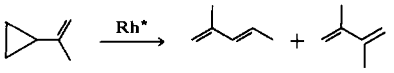
(180) (181)

The complex $[Rh(CO)_2Cl]_2$ was found to be highly efficient in the isomerization of VCP into 1,3-dienes [66–68].

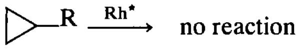




(62) (182)



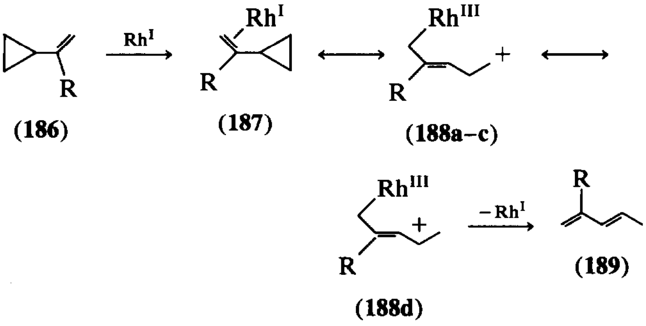
(183) (184) 90% (185) 10%



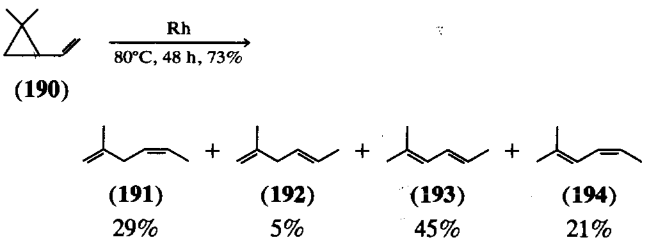
R = Me, Et

Rh* = $[Rh(CO)_2Cl]_2$, 90°C, $CHCl_3$

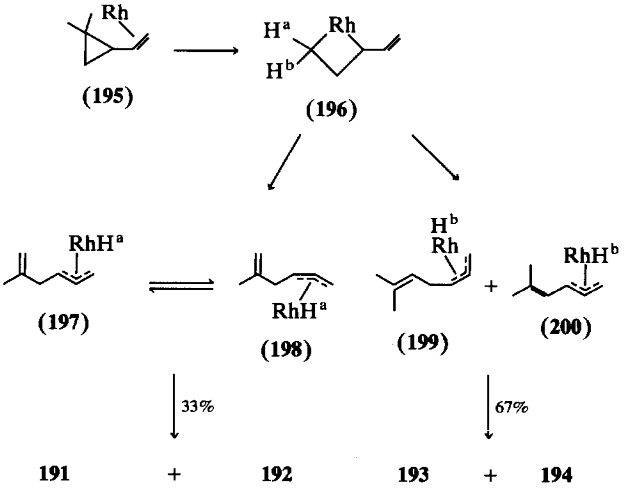
The intramolecular migration of hydrogen is shown by the absence of deuterium in the products of VCP isomerization conducted under gaseous deuterium or in $CDCl_3$. Since alkylcyclopropanes cannot be isomerized under otherwise similar conditions, the primary reaction step was assumed to be coordination of the VCP vinyl group at the Rh central atom. Accounting for the complexes' structures, Voigt *et al.* [69] suggested the following mechanism for the VCP isomerization where the key role was assigned to the Rh σ-alkyl complexes of **188a–d**.



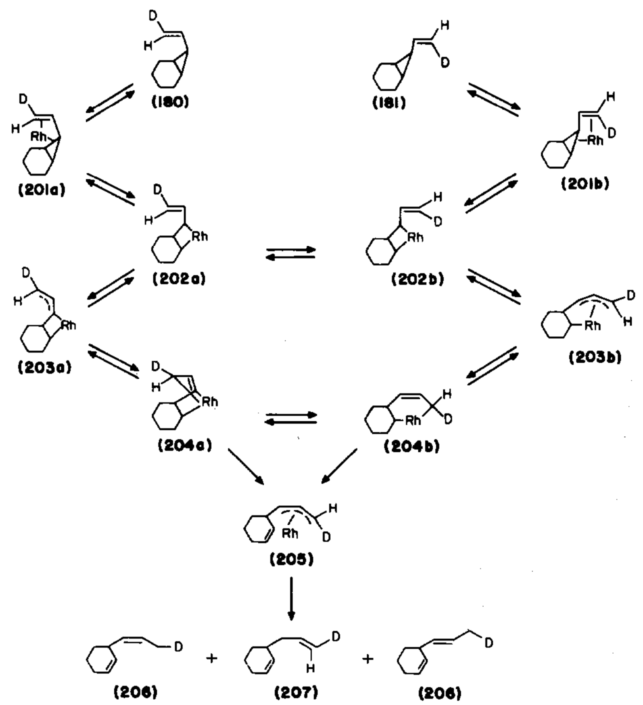
This scheme is not perfect because it fails to provide a rational explanation for the products of the isomerization of 1,1-dimethyl-2-vinylcyclopropane **190**, and particularly for 1,4-dienes **191** and **192** [66].



Powell *et al.* [66] suggested a different mechanism for the VCP isomerization, which accommodates the formation of both 1,3- and 1,4-dienes. The key role in the reaction was assigned to the Rh cyclobutane complex **196** formed after the inclusion of Rh^I into the three-membered ring.

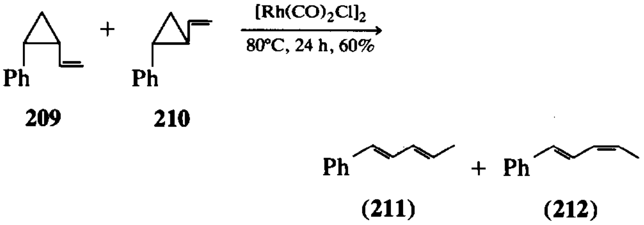


The hydride shift in **196**, can occur either from the *exo*-cyclic (H^a) or the *endo*-cyclic (H^b) position. Hence both 1,3-dienes and 1,4-dienes are formed. The *syn–anti*-isomerization of the vinyl group in VCP may occur through the Rh cyclobutane complex by the sequence **180** → **201** → **202** → **181**. The scheme below provides a complete and unambiguous representation of the mechanism of the VCP isomerization catalyzed by Rh complexes [65].



This reaction involves metal cycles of two equilibrated types **202a,b** and **203a,b**. Moreover, the equilibrium is maintained between the metal cycle **204a** and its isomer **204b** which has a more advantageous structure [65]. Therefore, the reaction scheme envisages the formation of a Rh cyclobutane complex as the key intermediate.

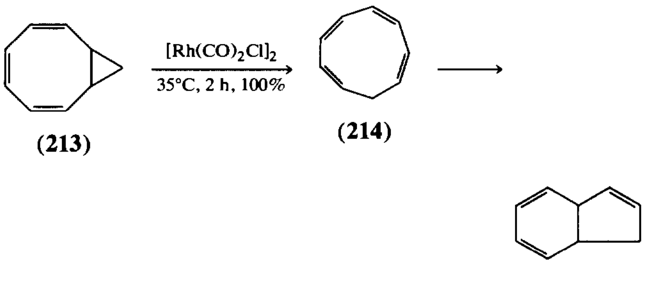
A mixture of *cis*- and *trans*-1-phenyl-2-vinylcyclopropanes **209** and **210** is isomerized into *E*,*E*- and *E*,*Z*-1-phenyl-1,3-dienes **211** and **212**, respectively, by a catalytic amount of the complex [Rh(CO)$_2$Cl]$_2$ [61,69].



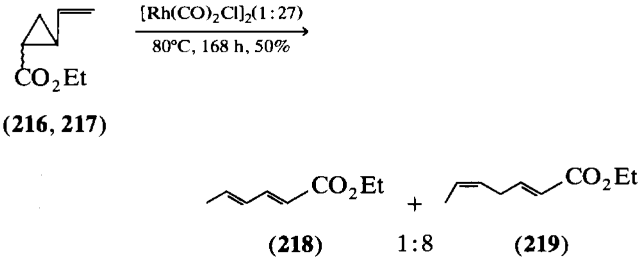
Neat *cis*-1-phenyl-2-vinylcyclopropane **209** is isomerized first into its *trans*-form **210** and then into the conjugated dienes **211** and **212** [65].

$$\mathbf{209} \xrightarrow[50\%]{[Rh(CO)_2Cl]_2} \mathbf{210}$$

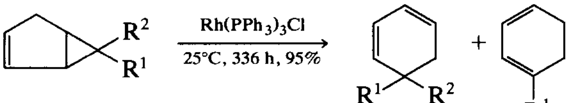
With the complex [Rh(CO)$_2$Cl]$_2$, bicyclo[6.1.0]nonatriene **213** containing a VCP fragment is rearranged to give *cis*-8,9-dihydroindene **215** [70].



The process was assumed to be stepwise, involving the catalytic isomerization of **213** into 1,3,5,7-cyclononatriene **214** and a subsequent pericyclic reaction of **214**, which led to the final **215** [70]. The catalytic reactions of VCP having electron-withdrawing substituents, were also studied. Thus, *cis*- and *trans*-1-carboethoxy-2-vinylcyclopropanes **216** and **217** were isomerized into a mixture of ethyl esters of 2*E*,4*E*- and 2*E*,4*Z*-heptadiene acids. The reaction was slow and required a good excess of the Rh-containing catalyst [65].



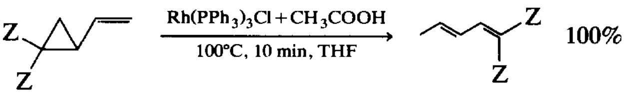
The bicyclic VCPs **220–223** with at least one electron-accepting substituent [71] were difficult to isomerize.



$R^1 = CO_2Me$	$R^2 = CO_2Me$	**(220)**	**(224)**	2:3	**(225)** ($R^2 = H$)
H	CO_2Me	**(221)**	**(226)**		
CO_2Me	Me	**(222)**	**(227)**		
Me	CO_2Me	**(223)**	**(228)**		

Oxygen promotes the reaction; the yield is increased and the reaction time was reduced to two days after bubbling of the reaction mixture with O_2 for 15–20 sec. The resultant catalyst turned out to be a peroxy-complex $Rh(PPh_3)_3Cl(O_2)$ [71]. With the complex $Rh(PPh_3)(CO)Cl$ the isomerization **220** → **223** needs as long as 30 days to complete [71].

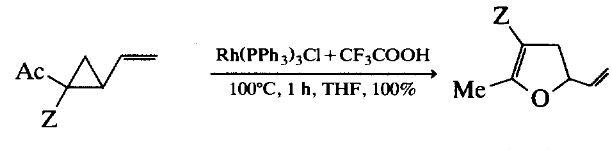
The activity of the Rh-containing catalysts was much increased by acidic promoting agents such as CH_3COOH or CF_3COOH (Rh : acid = 1 : 25) [42,72,73].



(229) **(230)**

Z = CO_2Me

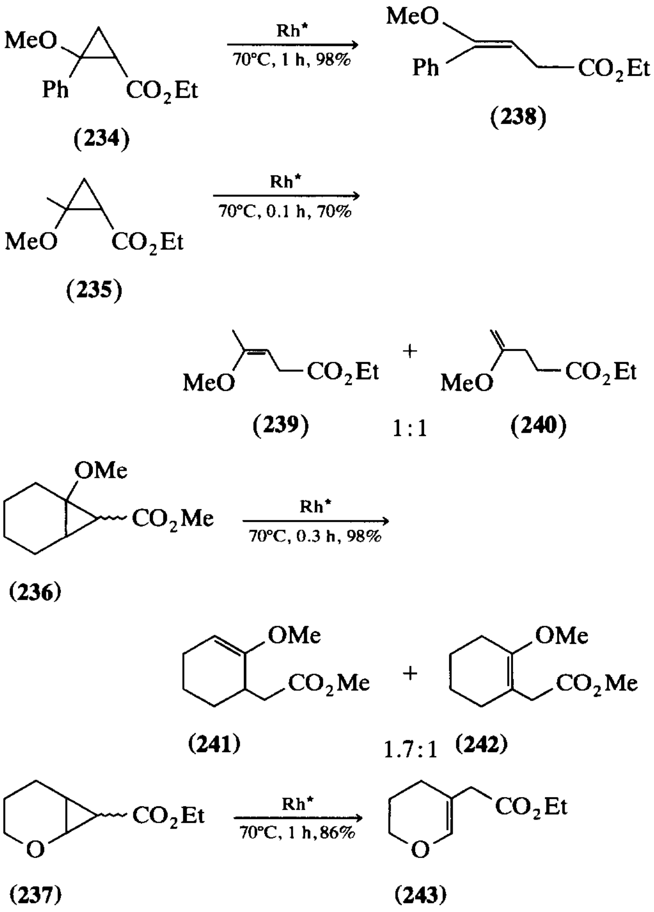
With at least one acetyl group in a VCP molecule as in **231** and **232**, the isomerization catalyzed by the system $Rh(PPh_3)_3Cl + CH_3COOH$ is diverted towards the formation of dihydrofurans **233** and **234** [73].



Z = Ac **(231)** **(233)**

CO_2Me **(232)** **(234)**

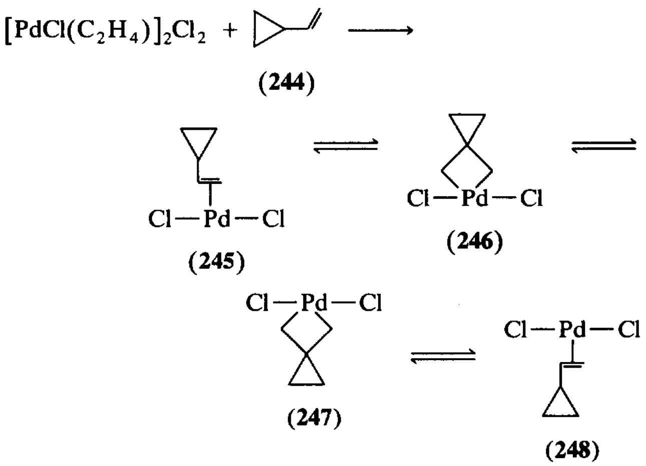
The behaviour of cyclopropanes **234–237** with functional 1,2-substituents, that have no vinyl groups is interesting. Their cyclopropyl-allyl isomerization was reported to be fast with either Rh-, Pt- or Cu-containing catalysts and required no promoting agents [74–78].



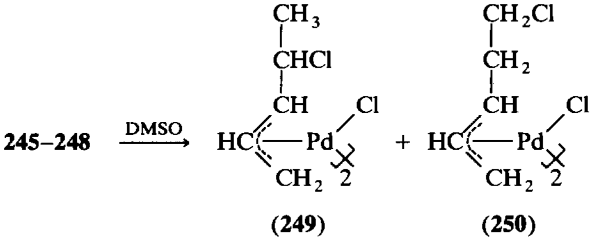
Rh* = $[Rh(CO)_2Cl]_2$

6. Catalysis by palladium complexes

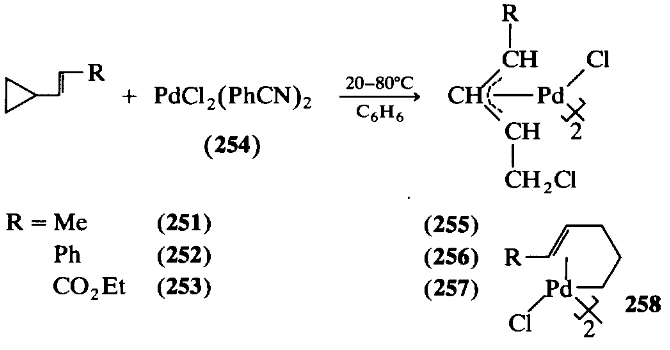
Vinylcyclopropanes easily form complexes with Pd compounds. For example, VCP **244** readily substitutes for ethylene in the palladium complex $[PdCl(C_2H_4)_2]Cl$ to give **248** [79–86]. The ^1H NMR spectrum of **248** showed a broad singlet in the region of 1.5 ppm, and the complex VCP-Pd was assumed to exist as several species **245–248**, equilibrating through 2,3-hydride shifts.



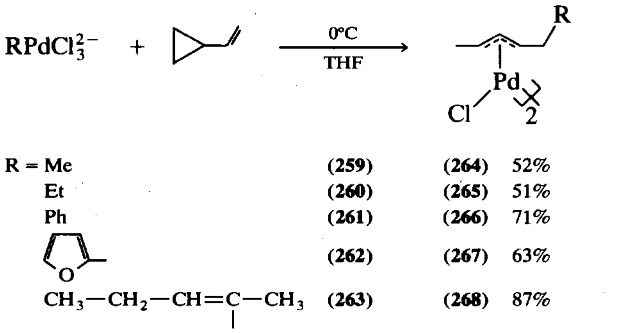
The complexes **245–248** are not stable. Treatment with DMSO, isomerizes them into a mixture of π-allylic derivatives **249** and **250**, with structures identical to those of the complexes obtained earlier from penta-1,3-diene and $PdCl_2$ [79,87–91].



The reactions of substituted VCP **251–253** with a Pd benzonitrile complex **254** gave straight away π-allylic complexes **255–257**, thus bypassing simple π-complexes [92–94].

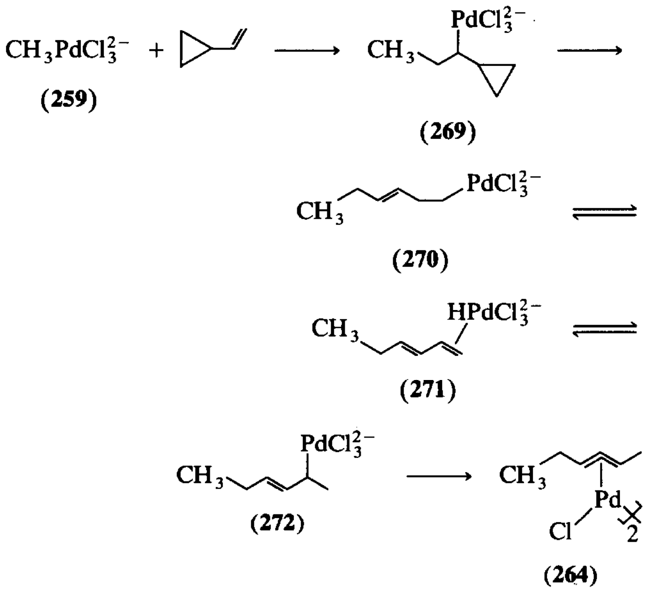


Dynamic NMR spectroscopy was used to identify an equilibrium between the Pd π-allylic complexes **255–257** and the related σ,π-complexes **258** [94]. The equilibrium was maintained in solution as well as in the solid state [95]. The reactions of VCP with Pd σ-alkyl (aryl) derivatives **258–263** were shown to provide a more convenient pathway to the Pd π-allylic complexes [92,96–98].

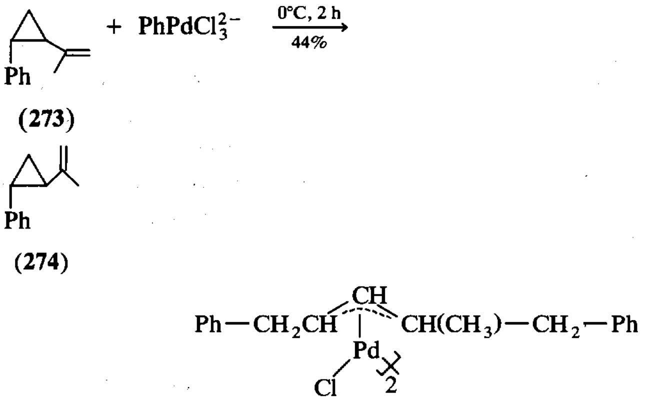


The required Pd alkyl(aryl) complexes **259–263** were synthesized from organomercury compounds, RHgCl, and Li_2PdCl_4.

The π-allylic complexes **264–268** were thought to be formed by carbometallation of the double bond in the VCP, followed by cyclopropylcarbonyl-homoallyl rearrangement of the Pd σ-complex **269** according to the following scheme [96]:



Similar transformations are also known for substituted VCPs [96]. Thus, *cis*- and *trans*-1-phenyl-isopropenylcyclopropanes **273** and **274**, respectively, react with $Li_2[PhPdCl_3]$ to yield the same π-allylic complex **275** having the structure of bis(2,4-η^3-1,5-diphenylhept-2-en-4-yl-palladiumdichloride) [96,99].

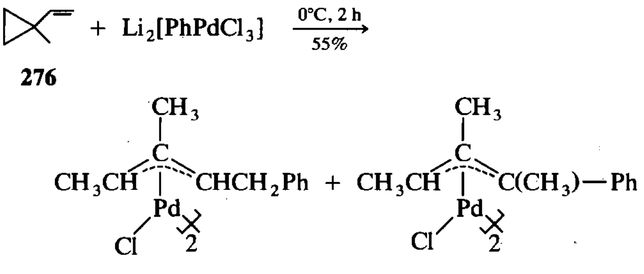


(273)

(274)

(275)

1-Methyl-1-vinylcyclopropane **276** reacts nonselectively with Li$_2$[PhPdCl$_3$] to give a mixture of two π-allylic complexes **277** and **278** [96,100].



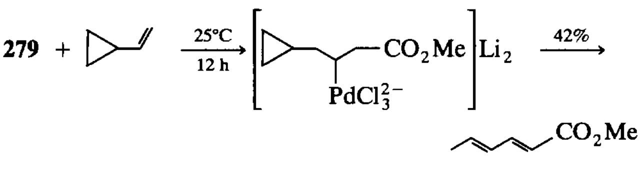
276

(277) (278)

The reaction of VCP with a carbomethoxypalladium complex **279** does not stop at the π-allylic complex, but goes on to yield methyl sorbate **280** [96].

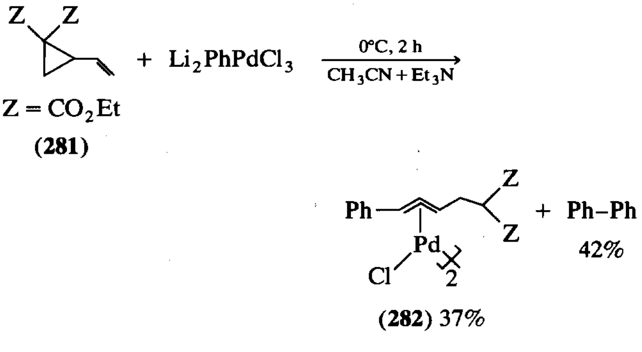
$$\mathrm{AcOHgCO_2Me} + \mathrm{Li_2PdCl_4} \xrightarrow[0^\circ\mathrm{C},\ 2\ \mathrm{h}]{\mathrm{CH_3CN}} \mathrm{Li_2[MeO_2CPdCl_3]}$$

(279)



280

The reactions of VCPs having polar substituents, with Li$_2$[PhPdCl$_3$], are more difficult to perform, hence the use of triethylamine as a promoting agent [99,101].

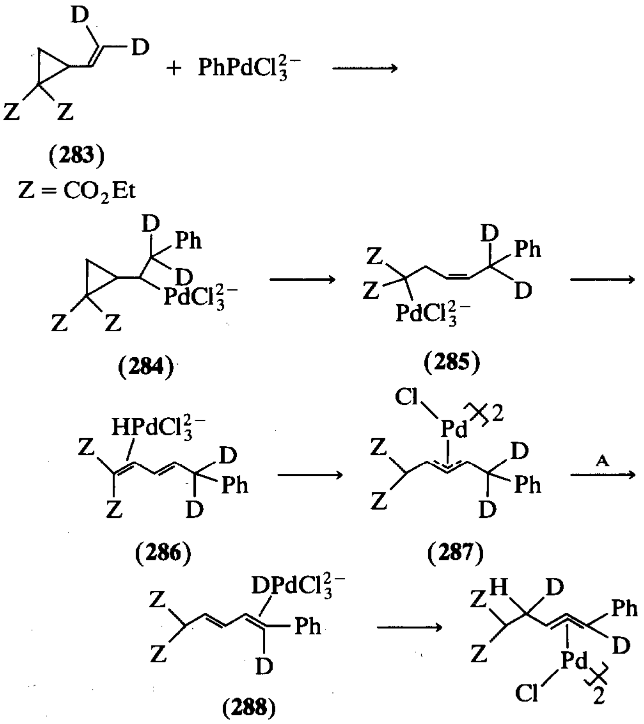


Z = CO$_2$Et

(281)

(282) 37%

To elucidate the mechanism of formation of the complex **282**, the reaction was carried out with a deuterium labelled VCP **283** and gave a complex **289**, showing deuterium at C^1 and C^4. The positional shift of deuterium was assumed to take place at step A next to the last one [95].



(283)

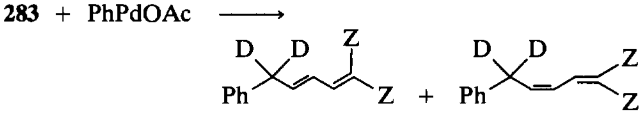
Z = CO$_2$Et

(284) (285)

(286) (287)

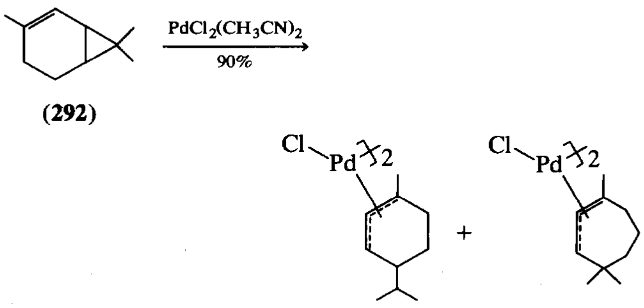
(288) (289)

Further evidence for the first three steps was provided by the reaction of **283** with phenylpalladium acetate in acetonitrile in the presence of Et$_3$N [95].



(290) 2:1 (291)

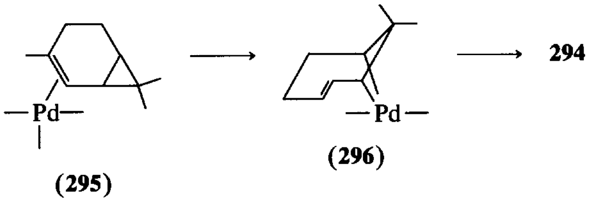
Bicyclic VCPs react in the presence of Pd compounds [88,89]. Thus, a mixture of two Pd π-allylic complexes **293** and **294** was obtained after treatment of carene-2 **292** with an equimolar amount of PdCl$_2$(CH$_3$CN)$_2$ [102].

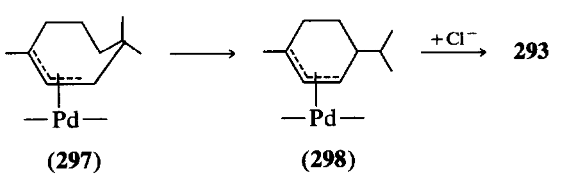


(292)

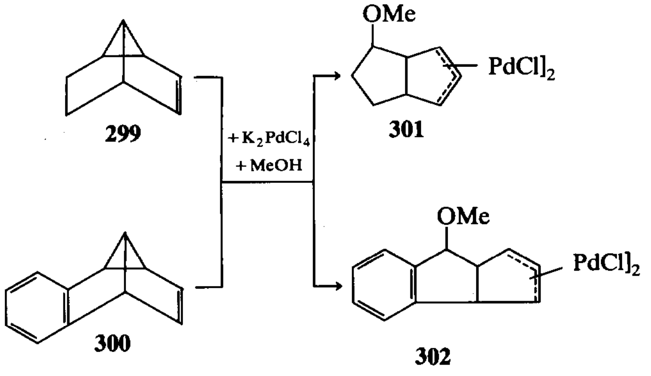
(293) (294)

Backvall [100] suggested that the formation of **293** and **294** proceeds through an intermediate Pd-cyclobutane **296**.

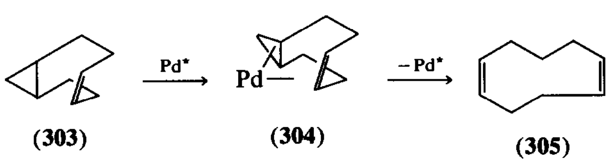




Reactions of semibullvalene **299** and benzobullvalene **300** with K_2PdCl_4 in methanol are rather complicated and the resultant π-allylic complexes **301** and **302** carry methoxy-groups [31].

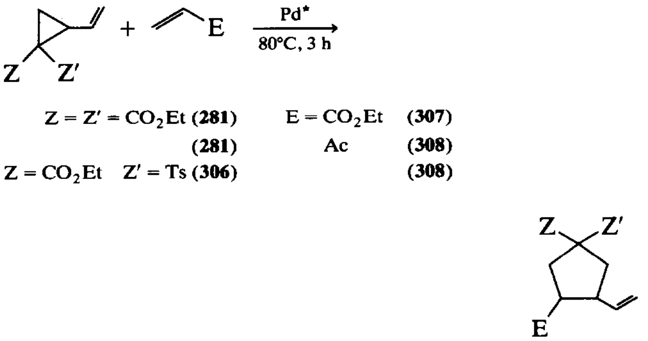


Albelo *et al.* [103] described a very specific reaction where a homoconjugated double bond activates the cyclopropane ring.



The structure of bicyclo[6.1.0]non-6-ene **303** favours chelated coordination of the CPR and a free double bond at the catalyst central atom (the complex **304**), and further isomerization of the three-carbon ring, which leads to expansion of the cycle.

Assisted by Pd^0 complexes, VCPs having electron-withdrawing substituents can undergo [3 + 2]-cycloaddition with α,β-unsaturated ketones and esters to yield cyclopentane derivatives [104–106].

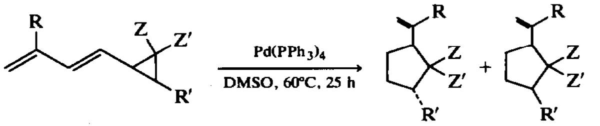


Z = Z′ = CO_2Et (**281**) E = CO_2Et (**307**)
(**281**) Ac (**308**)
Z = CO_2Et Z′ = Ts (**306**) (**308**)

(**309**) 84%
(**310**) 66%
(**311**) 77%

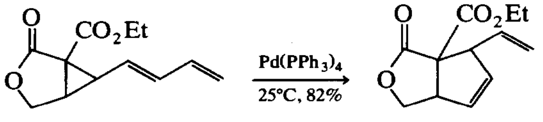
$$Pd^* = Pd_2(DBA)_3 \cdot CHCl_3 + Ph_2P(CH_2)_2PPh_2 \cdot DMSO$$

Cyclopentanes **312–320**, **322** and **324** were prepared also via isomerization of 1-cyclopropyl-substituted 1,3-dienes **311a–e**, **321** and **322** with Pd^0 complexes [107,108]. The VCP group in the 1,3-dienes was found to be responsible for the transformations.

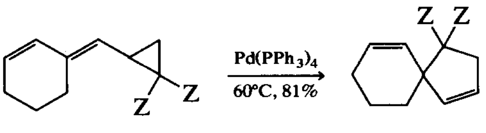


(**311a–e**)

a R = R′ = H Z = Z′ = CO_2Me	(**312**)	87%		0
b R = H R′ = Me Z = Z′ = CO_2Me	(**313**)	3 : 1	(**314**)	84%
c R = R′ = H Z = Ac Z′ = CO_2Me	(**315**)	1 : 1	(**316**)	96%
d R = R′ = Me Z = Ts Z′ = CO_2Me	(**317**)	1 : 1	(**318**)	89%
e R = R′ = Me Z = Z′ = CO_2Me	(**319**)	3 : 1	(**320**)	86%

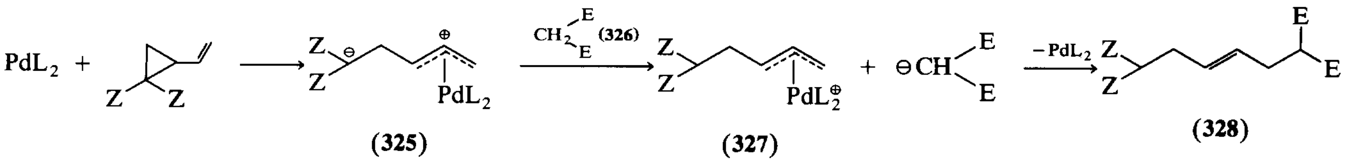


(**321**) (**322**)



(**323**) (**324**)
Z = CO_2Et

Palladium complexes were used to perform transformations of VCP previously activated by electron-withdrawing substituents [107,109–114]. In particular, conjugated addition of various CH-acids to the VCP was implemented successfully [107,114]. The reactions

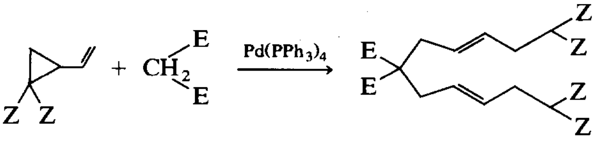


(325) (327) (328)

$Z = E = CO_2Me \quad L = PPh_3$

were considered to proceed through an intermediate zwitterionic Pd π-allylic complex **325**. The latter complex deprotonates a CH-acid substrate (*e.g.* an activated CH$_2$-group) to lead to an ionic pair **327**, and the reaction is complete with release of PdL$_2$, while the carbanion and the positively charged VCP fragment give the final product **328** [114].

An excess of **229** may result in doubly alkylated CH-acids.



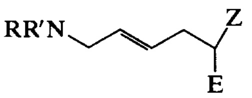
(229) (329)

This reaction involves the wide range of substituted VCPs **229**, **281**, **330** and CH-acids **326**, **331**, **332** [114].

It should be emphasized that the bicyclic VCP **342** and **343** result only in the [1 + 1]-products as **344–347** [107,114].

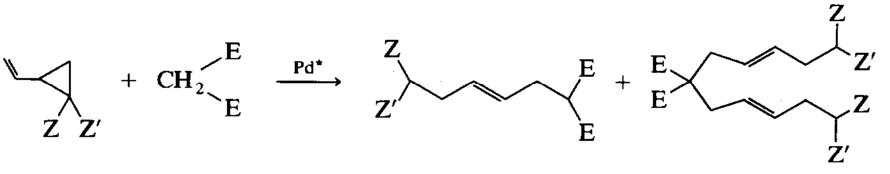
Secondary amines react with VCP in the same way as compounds with active CH$_2$-groups [113,115].

R = R' = Et	(348)	Z = E = CO$_2$Me
R = R' = -CH$_2$OCH$_2$-	(349)	CO$_2$Et
R = R' R' = Et	(350)	Z = CN E = CO$_2$Et
		Z = Ac E = CO$_2$Et



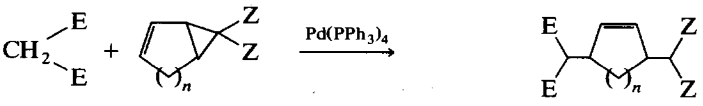
Z = E = CO$_2$Me	(351a–c)
CO$_2$Et	(352a–c)
Z = CN E = CO$_2$Et	(353a–c)
Z = Ac E = CO$_2$Et	(354a–c)

With 1,3-dienes as a further component in the reaction mixture conjugated amination occurs and octadienylation of the VCP [113,115].



Z = Z' = CO$_2$Me	(229)	E = Ac	(331)	(333)		1:2	(339)	89%
	(229)	1:1 Ts	(332)	(334)	94%			
	(229)	2:1	(332)				(340)	96%
Z = Z' = Ts	(330)	1:3 CO$_2$Me	(326)	(335)	18%			
CO$_2$Et	(281)		(326)	(336)	23%			
Ts	(330)		(331)	(337)		2:1	(341)	94%
	(330)	1:3	(332)	(338)	61%			

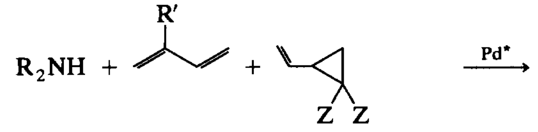
Pd* = Pd(PPh$_3$)$_4$, 20°C, 5–8 h



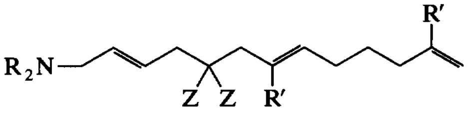
$Z = CO_2Me$

E = Ac (331)	n = 1 (342)
Ts (332)	2 (343)
CO$_2$Me (326)	1 (342)
Ts (332)	2 (343)

E = Ac	n = 1 (344) 89%	n = 2 (345) 84%
Ts	1 (346) 66%	2 (347) 46%
CO$_2$Me	1 (346) 84%	
Ts	2 (347) –	

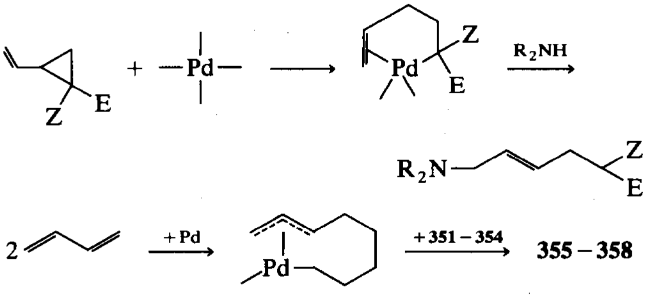


R = Et (**348**) R' = H, CH_3 Z = CO_2Et
$-CH_2OCH_2-$ (**349**)

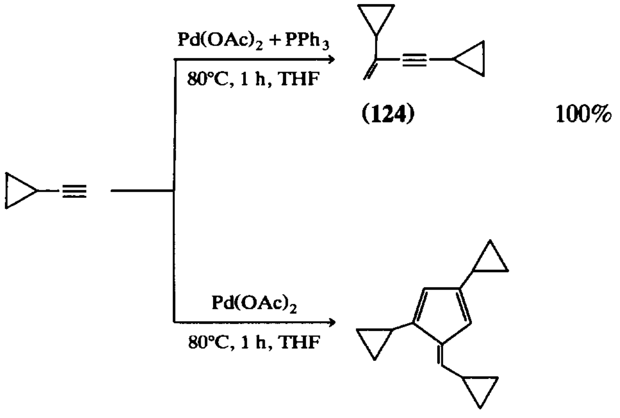


R = Et	R' = H	(**355**)	92%
Et	CH_3	(**356**)	50%
$-CH_2OCH_2-$	H	(**357**)	79%
$-CH_2OCH_2-$	CH_3	(**358**)	55%

The following reaction scheme provides an explanation for the structures of the products **355–358** [113,115].



Palladium complexes catalyze two attractive reactions with cyclopropylacetylene, *i.e.* linear dimerization and cyclotrimerization resulting in tricyclopropyl-substituted fulvene **359** [42,46].



(**124**) 100%

(**359**) 99%

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